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VOLUME XVI NUMBER 1

January, 1943

Published under the Auspices of the
DIVISION OF RUBBER CHEMISTRY
of the
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HARRISON E. HOWE

With the death of Harrison E. Howe, Editor of *Industrial Engineering and Chemistry*, in Washington on December 10, 1942, the Rubber Division has lost one of its strongest supporters and warmest friends. Every member regarded him, not only as a sponsor of the Division, but as a personal acquaintance. He was, perhaps, our most distinguished unofficial but honorary member. So great was his interest that he was always a genial fixture at the head table of Rubber Division banquets. Regardless of the pressure of many other demands at Society meetings, he considered these occasions a definite and, we hope, pleasurable obligation.

Dr. Howe occupied a distinguished position in the chemistry of the United States, and his reputation was worldwide. For twenty-one years he was Editor of *Industrial Engineering and Chemistry*. Under his leadership, this periodical expanded greatly. He raised it to the position of the most widely known and respected journal of industrial chemistry in the world.

He was also Editor of the Technologic Series of American Chemical Society Monographs, and the many volumes produced under this editorship added greatly to the chemical literature.

His place in American chemistry brought him many honors. He received four honorary Doctor's degrees, a foreign decoration, and the Chemical Industry Medal of the American Section of the Society of Chemical Industry. He was a member of many scientific organizations, and was extremely active in Rotary International.

Dr. Howe was born in Kentucky on December 15, 1881, and so was in his 61st year. He received his Bachelor's Degree from Earlham College in Indiana. He attended the University of Michigan, and received a Master's Degree from the University of Rochester. Previous to becoming Editor of *Industrial Engineering and Chemistry*, he was associated with the beet sugar industry, Bausch & Lomb Optical Company, and Arthur D. Little, Inc. In the first World War, he was a consultant to the Ordnance Department of the Army. In the present war, he was Chairman of the Chemicals Group of the Office of

Production Management in 1941, and later was Chariman of the Chemical Priority Advisory Committee of the War Production Board. These were but a few of his many activtiies in governmental and scientific organizations.

He did much to bring the realities of chemistry to the general public, both in his writings, and his many speaking engagements. As a speaker, he was in great demand, and never failed to provide a stimulating discourse.

The Rubber Division has, indeed, suffered a great loss.

J. T. BLAKE

WINFIELD SCOTT

The Division of Rubber Chemistry, through the death of Winfield Scott in Akron, Ohio, November 19, 1942, has lost one of its oldest, best liked and most respected members.

Scott was born in Senecaville, Ohio, on December 14, 1887. He completed his undergraduate work at Obelin College and received his masters degree from the University of Washington shortly before the First World War. Following a career in the Army, he became a research chemist in the laboratories of The Goodyear Tire & Rubber Company in Akron. He remained with Goodyear until 1920, when he went to the Quaker City Rubber Company in Philadelphia as a chemist and compounder; he remained with that concern until 1922. For the following two years he was employed by the Rubber Chemicals Division of E. I. du Pont de Nemours & Company of Wilmington, Delaware. From 1924 to 1929 he was in charge of all research work for the Rubber Service Laboratories at Nitro, West Virginia.

In 1929, in company with C. O. North, he founded the Kavalco Products Company of Nitro, West Virginia, where he remained until 1933, when he returned to Goodyear. Since that time he has been engaged in chemical research work with The Goodyear Tire & Rubber Company.

Scott has written numerous articles on vulcanization accelerators and antioxidants of rubber, and holds many patents on such compounds. He was considered an authority on the theory of vulcanization. In company with C. W. Bedford, Scott published the first papers on the mechanism of the accelerated vulcanization of rubber. He has approximately ninety issued patents, and a large number still pending in the Patent Office.

All who knew "Scotty" will remember him for the thoroughly human and friendly nature of his character. He was always a gentleman, and was always ready to share his wit and humor with others. He possessed the ability to accept adversities in life and still remain cheerful. He sought no credit or glory in his achievements, but the achievements linked with his name will forever stand in the records of the progress of rubber chemistry.

He was a member of the American Chemical Society, the American Institute of Chemical Engineers, the Franklin Club, Sigma Xi, and Phi Lambda Upsilon. He was immediate past chairman of the Akron Section of the American Chemical Society.

Besides his wife, two daughters and a granddaughter, Winfield Scott is survived by his mother, sister and brother in Philadelphia, Pennsylvania.

L. B. SEBRELL

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NEW BOOKS AND OTHER PUBLICATIONS

KOK-SAGYZ, FAMILY COMPOSITAE, AS A PRACTICAL SOURCE OF NATURAL RUBBER FOR THE UNITED STATES. Paul J. Kolachov. National Farm Chemurgic Council, 50 W. Broad St., Columbus, O. 20 pages. Price 25c.—This pamphlet contains a good survey of the history, cultivation, and economic aspects of the possible use of *kok-sagyz* as a source of natural rubber for the United States. The material for this article was obtained from recent literature on this subject from Russia, and the author strongly recommends active research on the cultivation of this plant. [From the *India Rubber World.*]

EXTRACTION OF RUBBER FROM PLANTS. Muriel E. Whalley. National Research Council of Canada, Ottawa, Ont., Canada. 19 pages. Price 25c.—This report resulted from a search of the literature on this subject in *Chemical Abstracts* and numerous other books, pamphlets, etc. It is divided into three sections: (1) in which original articles are reviewed in detail, (2) in which references are listed, and (3) in which other material of which complete articles were not readily available is presented in the form of abstracts. [From the *India Rubber World.*]

A SUMMARY OF DATA ON RECLAIMED AND SCRAP RUBBER. The Rubber Manufacturers Association, Inc., 444 Madison Ave., N. Y. 26 pages.—This bulletin, designed primarily for writers on the subject of rubber, is a digest of information on scrap and reclaimed rubber that has appeared in various publications. A list of sources for additional data is given. The bulletin represents a very useful source of information on these subjects as regards processes, historical background, statistics, and current events up to August, 1942. [From the *India Rubber World.*]

BUTYL RUBBER—MANUFACTURE OF TIRES AND INNER TUBES. Stanco Distributors, Inc., 26 Broadway, New York, N. Y. 8 pages.—This pamphlet gives latest processing details of the use of Butyl rubber for tires and cover stocks for carcass, beads, and treads, with representative compound formulas in the appendix. Information on tire building, construction, bagging, and curing gives the best technique for these operations and mentions that procedures outlined may be conservative and more time-consuming than ordinarily desired, but are given as a sure way to obtain satisfactory results and are open to improvement. A faster rate of production may be realized as more experience and knowledge are gained in handling larger volumes of this rubber. In a similar way the manufacture of inner tubes, including tubing and splicing, and a recommendation for attaching valves with Butyl rubber valve-pads is included. A section on quality explains the results of tests on Butyl rubber tires and tubes in relation to the basic properties of this type rubber and present methods of manufacture of these products from it. A review of the precautions necessary in factory-processing of Butyl rubber and a short discussion of cured properties are also given. [From the *India Rubber World.*]

ELECTROPHORESIS OF PROTEINS AND THE CHEMISTRY OF CELL SURFACES. Harold A. Abramson, Laurence S. Moyer, and Manuel H. Gorin. Published by Reinhold Publishing Corp., 330 W. 42nd St., New York, N. Y. 1942. Cloth, 9¼ x 6¼ inches, 341 pages. Price $6.—The isolation of single proteins from complex natural mixtures for intensive study is an important function of electrophoresis experimentation, which also has proved an effective method of investigating the behavior of proteins at surfaces and in solutions. In this volume the results of investigations by both the moving boundary and the microscopic method are correlated, and the data applied to study of the surfaces to blood cells, the skin, bacteria, latex, etc. The theoretical discussion is prefaced by an elementary presentation of the general principles of electrophoretic migration in liquids, and brief chapters on the historical background, and methods. The book is primarily of interest to those workers investigating the surface chemistry of living cells.

The chapter on latex discusses the surface chemistry of latex particles and describes the behavior of the proteins of *Euphorbia* and *asclepias* latices. [From the *India Rubber World.*]

THE STORAGE OF 1,3-BUTADIENE. Pittsburgh-Des Moines Steel Co., Pittsburgh, Pa. 36 pages.—This research bulletin is a report on the work done under a Chemical Storage Fellowship at the Mellon Institute of Industrial Research for the above company. The report contains new information and data on variables which affect storage costs, recommendations for type of storage containers, cost data, information regarding corrosive effects on container materials, and deterioration of butadiene during storage. A section on physical constants includes data and charts on specific gravity, specific heats, vapor pressure, and latent heat of vaporization. Sections on chemical properties and methods of preparation give information on catalyzers, inhibiters, and modifying agents in the former, and a review of the most generally accepted methods in the latter. A table of literature references is also included. [From the *India Rubber World.*]

LIMITS OF INFLAMMABILITY OF BUTADIENE IN AIR. (R. I. 3565.) G. W. Jones and R. E. Kennedy. Bureau of Mines, Department of the Interior, Washington, D. C. 8 x 10½ in. 6 pp.—To answer inquiries that have been received by the Bureau of Mines as to the explosive hazards of butadiene, the combustible gas used in most of the synthetic rubber processes, and its limits

of inflammability in air have been determined, and the results are given in this research report. Test procedures are described, and apparatus used is illustrated. [From *The Rubber Age* of New York.]

THE NEOPRENES. E. I. du Pont de Nemours & Co., Inc., Wilmington, Del. 24 pages.—This booklet, by D. F. Fraser and N. L. Catton, provides under one cover a listing and description of all types of Neoprene now being manufactured, with a primary classification into slow-curing and fast-curing types. The general principles of compounding these rubbers is given, and also compounding for specific applications, such as freeze-resistance, flame-resistance, sunlight- and ozone-resistance, oil-resistance, low compression-set, and high tensile strength. The processing of Neoprene compositions and their methods of vulcanization are also explained, and the booklet includes a literature reference on Neoprenes which covers previous publications of the company's staff and other authors on this subject. [From the *India Rubber World.*]

RESINS—RUBBERS—PLASTICS. Loose-Leaf Abstract Service. Edited by H. Mark and E. S. Proskauer. Interscience Publishers, Inc., 215 Fourth Ave., New York, N. Y. Price $35.00 per year. 6½ by 9½ inches in binder. 400 pages (through September).—This monthly service, started with January, provides a close check-up of the scientific and technical literature so necessary to avoid loss of time and money by duplication of work already described. It should be invaluable to executives, research chemists, and engineers, in fact to all workers in these fields, particularly during this period when time is so short.

The abstracts are prepared in a very comprehensive manner in that they contain most of the data and facts of the original paper and reproduce important graphs, diagrams of apparatus, and other necessary illustrations; in most cases it would not be necessary to consult the original literature. The service will furnish about 1,000 abstracts a year, summarizing articles from more than 100 domestic and foreign periodicals and will, therefore, cover the entire field of chemistry, physics and technology of resins, rubbers, plastics and high-polymeric substances. Each abstract is provided with a file number. An index to a specially adapted decimal system and method of filing gives two main headings: General and Special. The first will include division and classification into the various fundamental properties and process of these materials and will combine all information that does not refer to a specific chemical compound or group of substances. The Special Part will be divided into sections on various substances or substance groups, such as resins (acrylic, phenolic, vinyl, shellac, and natural), rubbers (natural, butadiene, chloroprene, polysulfide, vinyl, isobutylene), and fibers (cellulose, protein, Nylon, Vinyon). If an article contains heterogeneous material, several abstract sheets are made, each of which deals with only one topic of the article, but all of which are cross-referenced.

The service provides an up-to-date reference library in which every recent development can be found at a moment's notice. [From the *India Rubber World.*]

PLASTICS. J. H. DuBois. Published by American Technical Society, Drexel Ave. at 58th St., Chicago, Ill. 5½ x 8¼ in. 291 pp. $3.00.—This book is a simplified presentation of the manufacture and use of the more important plastics materials and products, with tables of their properties and the basic design information required by engineers and designers. It omits formal chemistry as such, but explains in layman English what happens when

various materials are handled in certain manners, or, in other words, the production of plastics. It is primarily intended for the user of plastics rather than the chemist or research laboratory. It has been written to serve as a textbook for wide-awake schools whose aim is to prepare their students to meet the problems of industry.

The book has thirteen chapters in all, as well as a detailed subject index. Special chapters are devoted to a discussion of the phenolic, urea or amino, cellulose, acrylic, vinyl and styrene, cast phenolic and protein plastics. Others cover laminated plastics, compression and transfer molding, injection molding and continuous extrusion, finishing and decorating plastic products, and the design of molded products. A brief description of some of the better known synthetic rubber-like materials is included, with a table giving the properties of these materials. [From *The Rubber Age* of New York.]

PLASTICS FOR INDUSTRIAL USE. John Sasso. Published by the McGraw-Hill Book Co., Inc., 330 West 42nd St., New York, N. Y. 6 x 9 in. 229 pp. $2.50.—This is an engineering handbook of plastic materials, and methods for their use. Written from the engineers' standpoint, chemistry, except as it affects strength or performance, has not been included. Emphasis is placed on comparative properties, methods of selection for specific uses, and proper design. There are 17 chapters, early chapters giving the basic information needed before any plastic can be adapted to engineering use and the subsequent chapters devoted to specific plastics, with practical information on the properties of that particular plastic. The appendix consists of a directory of trade names, suppliers and molders. A comprehensive subject index is included. The author, incidentally, is associate editor of *Product Engineering*. [From *The Rubber Age* of New York.]

VINYLITE RESINS. THEIR FORMS, PROPERTIES, AND USES. Carbide & Carbon Chemicals Corp., 30 E. 42nd St., New York, N. Y. 20 pages.—The purpose of this booklet is to acquaint industry's executive and technical men with the wide range of useful properties of the Vinylite resins and the forms in which they are produced. Under copolymer resins, in addition to a table of general resistance properties, are descriptions of the use of these resins for surface coatings, as rigid sheets, and as plasticized sheeting and film. Molding and extrusion compounds are divided into two classes, rigid compounds and elastomeric compounds, and a table shows applications of both of these types for specific purposes. Sections on special Vinylite copolymer products, Vinylite polyvinyl butyral, polyvinyl acetate, and polyvinyl chloride resins conclude the booklet. [From the *India Rubber World*.]

STRATEGIC MATERIALS IN HEMISPHERE DEFENSE. M. S. Hessel, W. J. Murphy, and F. A. Hessel. Published by Hastings House, 67 W. 44th St., New York, N. Y. 1942. Cloth, 8¼ by 5½ inches, 235 pages. Bibliography. Price $2.50.—The sources, potential sources, needs and uses, of 14 strategic and 15 critical materials from the Army's list for hemisphere defense are surveyed in this study of the supply of essential things. At the head of the list are rubber and tin, which the authors call "pearls of great price lost in the Far East". The facts and figures on rubber are those which have been stated and often reiterated in the press during the last ten months, and similar conclusions also are drawn. South and Central American sources of supply of many of our essential needs are briefly discussed. The growth of the American chemical industry and its current rapid expansion, and the importation and synthesis of fats, oils, and gums are surveyed in relation to the war program.

From the correlation of facts and figures, it is obvious that the tremendous natural wealth of the United States is insufficient to win the war without tapping new sources of supply. After victory is won, the authors conclude, hemisphere autonomy developed by the emergency will have a large influence on United States prosperity and on world-wide trade and international economy, since we will no longer depend wholly on sources outside the Western Hemisphere for many raw materials. [From the *India Rubber World.*]

PATENTS AND INDUSTRIAL PROGRESS. George E. Folk. Published by Harpers & Brothers, 49 E. 33rd St., New York, N. Y. 1942. Cloth, 8½ by 5¾ inches, 393 pages. Price $3.—Patent cases presented to the Temporary National Economic Committee by the Departments of Justice and Commerce are summarized, analyzed, and evaluated, and legislative recommendations of the Committee based on governmental department proposals are presented in this study of timely interest to inventors and manufacturers. Charges against the patent system and alleged abuses of patent rights are clearly stated, as well as authoritative testimony showing the value of the system under which an industrial progress, unequalled in history, has been achieved in the United States. Cases cited include one in which Charles Goodyear was involved in 1869, and others concerning rubber patents.

The author has had over 40 years' experience in patent law. [From the *India Rubber World.*]

COMMODITY STATISTICS (1942). Prepared and published by the Commodity Research Bureau, Inc., 82 Beaver St., New York, N. Y. 8½ x 11 in. 294 pp. $5.00 (Combination price for both volumes, $10.00).—The Commodity Research Bureau is now offering its Commodity Year Book series, established four years ago, in two separate volumes, one termed the *Commodity Year Book* (*Master Edition*) and the other *Commodity Statistics*. The latter is, in reality, the 1942 Commodity Year Book, and is the fourth annual edition of this standard reference work.

The *Master Edition* represents a commodity encyclopedia. Whereas the preceding volumes of this excellent work on commodities were confined to discussions on background, processing and marketing of 75 basic commodities, with comprehensive statistical sections on each, the *Master Edition* has gone considerably further and covers virtually all the important raw and semi-finished products that serve to make up our national economy. There are separate articles on 836 different commodities which are the basis of military and civilian maintenance, with such detailed information as physical analysis, source of production, principal uses and finished products, actual and possible substitutes, and importance in the war effort.

This edition stresses the tremendous advance which has been marked by various synthetics, and points out how substitute materials have been used to excellent advantage. In the discussion on synthetic rubber, which occupies five pages, the editors take a very optimistic view of the future as regards supplies. Buna, Butyl and Neoprene are discussed at length. A detailed analysis of the plastics industry, prepared with the coöperation of the Society of the Plastics Industry, which explains molding and fabricating methods and presents authoritative data on each of the plastic types, is included.

The second volume, *Commodity Statistics*, will enable those who have purchased previous Year Books to have up-to-date figures for most of the statistical tables published in previous editions. With the country at war, certain information and statistics are naturally withheld from publication and accord-

ingly, as in the case of rubber, the statistical tables are mainly duplicates of those in the previous edition. [From *The Rubber Age* of New York.]

TWENTY-THREE WAYS TO CONSERVE THE LIFE OF YOUR MULTIPLE V-BELT DRIVES. Multiple V-Belt Drive Association, 140 S. Dearborn St., Chicago, Ill. 8½ x 11 in., 16 pp.—This book is a contribution to the rubber conservation movements, and its sole purpose is to educate power users in the proper procedure of selection, installation and maintenance of multiple V-belt drives to obtain maximum life from every belt. It is not an academic engineering handbook, but rather a primer on the subject, written and illustrated in a simple, easy-to-understand manner. [From *The Rubber Age* of New York.]

A.S.T.M. STANDARDS ON TEXTILE MATERIALS. Published annually by the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa. October, 1942. Paper 6 by 9 inches, 440 pages. Indexed. Price $2.25.—This publication, issued annually under the sponsorship of A.S.T.M. Committee D-13 on Textile Materials, gives in their latest form each of the 73 standards on textile materials, as developed through the work of this Society. Of special note is the information given in a 15-page section of photomicrographs of common textile fibers, information on basic properties, yarn-number conversion table, table for relative humidity, and an important glossary of terms relating to textile materials, which includes a discussion, with illustrations of defects in woven fabrics, and definitions. Of the 73 specifications and tests, 19 cover cotton and cotton goods, nine cover rayon, and 10 cover wool and wool yarn. Other widely used standards cover asbestos, glass, and other miscellaneous materials such as single jute yarn, jute rove and plied yarn (electrical purposes), lime for textile purposes, household blanketing, and electrical insulation (thickness). Sixteen of the standards are general in nature, and cover testing machines, fibers (identification and determination), fire-retardant properties, evaluating compounds for insect resistance, resistance to water, finishes on textiles (identification), and resistance to microorganisms.

Included is a list of papers on textiles presented before the Society or at meetings of Committee D-13, and there are abstracts of three recent papers involving statistical methods or technique in testing as related to this field. [From the *India Rubber World.*]

CHARACTER OF THE THERMAL MOTION OF LONG ORGANIC CHAINS, WITH REFERENCE TO THE ELASTIC PROPERTIES OF RUBBER *

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I. INTRODUCTION

Criticism of the Theory of Mark and Kuhn

The nature of the thermal motion of long-chain molecules has been the subject of numerous theoretical and experimental investigations during the last few years. This motion is a decisive factor in a wide variety of phenomena, particularly in connection with high molecular-weight polymers. The diffusion and viscosity in solution of chain molecules of both high and comparatively low molecular weights depends entirely on the structure which the chains take on in solution. In the last analysis, this structure is the result of the thermal motion of the chain. The dielectric constant, the kinetics of various reactions, the structure and properties of monomolecular films, the coagulation of solutions of high polymers, and, in fact, the properties of high molecular substances in the solid state, such as the remarkable mechanical properties of rubber and of its analogs, must to a large extent depend on the nature of the thermal motion of the molecules. At the present time, the interpretation of Mark[1] and Kuhn[2] is most widely accepted. The basic postulate of this theory is the assumption that free rotation may occur around single bonds, unless of course this results in a deformation of the angles between valences.

According to Mark and Kuhn, all angles of rotation are equally probable for an organic chain which possesses full freedom of rotation. An isolated chain, therefore, has the configuration of an elliptical ball, composed of a tangled molecule, which fills the interior of an ellipsoid of revolution, the length of which is equal to approximately 2.5 times the diameter.

The Brownian movement of a ball of this character can be analyzed in detail. For the average squared length of such an elliptical molecule, *i.e.*, the mean squared distance between the ends of the chain, Kuhn obtained the following expression:

$$\overline{\lambda^2} = nl^2 \frac{1 + \cos \omega}{1 - \cos \omega}$$

where n is the number of links in the chain, ω is the angle between the directions of the valences of the carbon atoms, and l is the length of each link.

Hence, in solution, even a very large molecule, with a chain of 1000 links, will have an average squared length of only 45 l. This means that such a molecule loses to a large extent its spacial asymmetry. On the basis of such representations, Mark and Kuhn attempted to explain the behavior of high-molecular systems. Of particular interest is their explanation of the elastic

* Translated for Rubber Chemistry and Technology by Leon Talalay from *Journal of Experimental and Theoretical Physics* (*U.S.S.R.*) **9**, 1094–1106 (1939).

properties of rubber. They analyzed the deformation of an isolated chain, and concluded that the deformation does not depend on a change in potential energy of the system, but is due to a change from the statistically more probable to the less probable configuration, resulting in a rise in entropy of the system. This gives rise to counteracting forces, and ultimately results in a definite value of the Young modulus. In this respect the elongation of rubber is quite analogous to the isothermal compression of an ideal gas. The extending force can be expressed by a relation closely resembling the Clapeyron equation:

$$\sigma = \frac{3}{nl^2} \frac{1 - \cos \alpha}{1 + \cos \alpha} \Delta l k T$$

where σ is the tension, and Δl is the elongation.

The crude representation described above does not take into account a number of important factors. It assumes no interaction between chains, nor does it allow for the crystallization which occurs when rubber is stretched. In vulcanized rubber, separate chains are linked together by sulfur bridges, with formation of large molecules. As a result, one can speak only of free sections of the chain, the length of which is only about 100–300 links, whereas the total length is about 1000–3000 links. Nevertheless, on the basis of his model, Kuhn obtained an absolute value of Young's modulus which was of the correct order of magnitude. Notwithstanding this, it must be said that the validity of such an explanation of elasticity is disputable. Actually the phenomenon of elastic deformation of a high molecular substance consists probably of two stages. First there is a change in the geometric configuration of individual molecules; secondly, there is a displacement of their centers of gravity, whereby the density of the substance does not change appreciably (Poisson's coefficient = 0.5). Without such displacement the tremendous deformations observed experimentally would be impossible. After removal of the strain, the substance returns to its original shape, *i.e.*, all points resume their starting position. The existence of such "rigidity of form" can evidently not be explained merely by the use of a statistical picture, where the chain coils up as a result of thermal motion. Without taking into account the action of molecules on each other, it is impossible to describe accurately the displacement of the centres of gravity of the parts, and no truthful picture of deformation can be obtained.

In the present article, neither the experimental background of the theory of Mark and Kuhn nor the application of the theory to various detailed processes is discussed. Rather the discussion is confined to a study of the basic physical concepts which form the origin of the theory in the light of new facts discovered recently.

It can be stated that, even in a single isolated chain, forces must be present which tend to hamper free rotation.

If the distances d_1 and d_2 between two neighboring hydrogen atoms, and also the distances D_1 and D_2 between two remote carbon atoms (really between CH_2-groups) in the *cis*- and *trans*-configurations of an ordinary aliphatic chain are calculated (see Figures 1 and 2), the following d_1 and D_1 values are obtained:

$$d_1 = 2.27 \text{ Å}; \quad d_2 = 2.52 \text{ Å};$$
$$D_1 = 2.52 \text{ Å}; \quad D_2 = 3.80 \text{ Å}.$$

In both cases, the distances are smaller than the so-called "gas-kinetic" diameters. For an atom of hydrogen, this is calculated to be, according to London[3]: $d = 3.5$ Å.

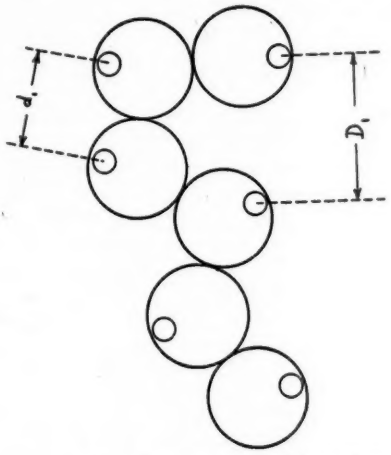

FIG. 1.—*Cis*-configuration of an aliphatic chain.

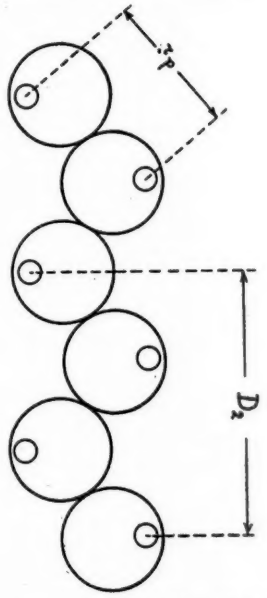

FIG. 2.—*Trans*-configuration of an aliphatic chain.

The diameter of a CH_2 group can be determined from crystal lattices, from the density of liquid hydrocarbons, or from data on monomolecular films. In every case the value obtained is approximately $D = 4.5$ Å.

It appears that, in a chain, H atoms as well as C atoms (or whole CH_2 groups) which are not chemically linked are too close together. Such atoms

are in a state of compression, and repel each other, with resulting strain in the chain. There is a gain in energy if the chain changes over from the *cis*-configuration (bent chain) to the *trans*-configuration (straight chain). This chain behaves like an elastic band or, rather, like a system of hinged rods which are pulled apart by springs. The individual rods are capable of a certain amount of twisting, but are not capable of free rotation at the hinges.

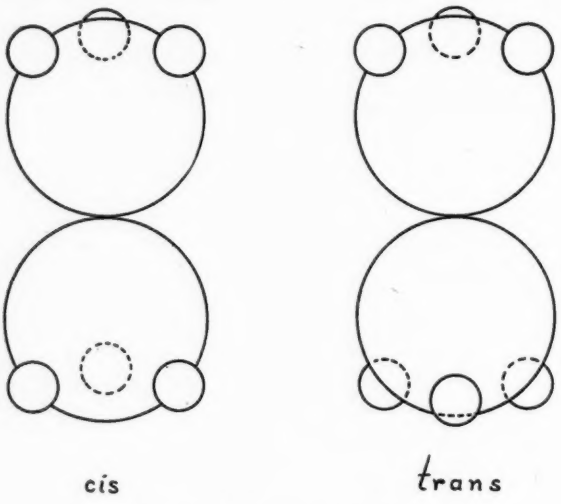

FIG. 3.—*Cis*- and *trans*-configurations of ethane.

Definite and, moreover, quantitative experimental confirmation of the above picture has been established by two investigators—Kistiakowsky[4] and Pitzer[5] independently of each other. They investigated the heat content of ethane at low temperatures (down to liquid-air temperatures). At such temperatures, vibrational degrees of freedom are practically nonexistent, and thus the question of freedom of rotation can be solved.

Figure 3 is a schematic diagram of the *cis*- and *trans*-configurations of ethane.

The only forces active in this case are the repulsion forces between H atoms. Pitzer and Kistiakowsky were able to show that these forces may be large. The energy difference between the two modifications is 3000 calories per mole, *i.e.*, corresponding to approximately 5 kT at normal temperature.

More recently, Kistiakowsky and collaborators[6] studied propane. They showed that, as before, free rotation does not take place. The *trans*-configuration is more stable, and the *cis*-configuration corresponds to a maximum of potential energy. The *cis*-state has a peak of activation which has to be overcome before oscillation around the equilibrium *trans*-configuration can be changed to free rotation.

The energy difference between the two states, *i.e.*, the activation energy difference between the stable and unstable state was found to be 3600 calories per mole, or approximately 6 kT.

The above principle of minimum energy can be applied to the thermal motion of an individual organic chain.

The change from *trans-* to *cis*-configuration is one of the links of the chain, and results in a bending of the chain at an angle of approximately 60°. It is quite justifiable, therefore, to represent the energy of the chain as a function of the angles between the planes passing through a pair of neighboring links. This function would be:

$$U = \frac{U_0}{2}(1 - \cos\theta), \tag{1}$$

where U_0 is of the order of $6\,kT$ at normal temperatures, and θ can change between 0 and π. Of course a sharp bending of the chain, as shown in Figure 1, is hardly probable. The total deformation of the chain is made up of a series of small angles between consecutive links of the chain. In view of the considerable length of the chain, however, the sum of the deformations may be large. The average statistical length of the molecule, by which is meant the mean square distance between the ends of the chain, differs considerably from the actual geometric length.

II. PROBLEM IN A SINGLE PLANE

The problem is first to find the average statistical length of a chain in the case of an individual isolated molecule (in dilute solution). To simplify the case, let one confine himself to two dimensions, *i.e.*, to configurations of our hinged molecule which lie in a single plane only. Suppose that the two neighboring links k and $k+1$ of the chain form an angle ϕ_k with each other.

The length of each link is 1, and the total number n (Figure 4).

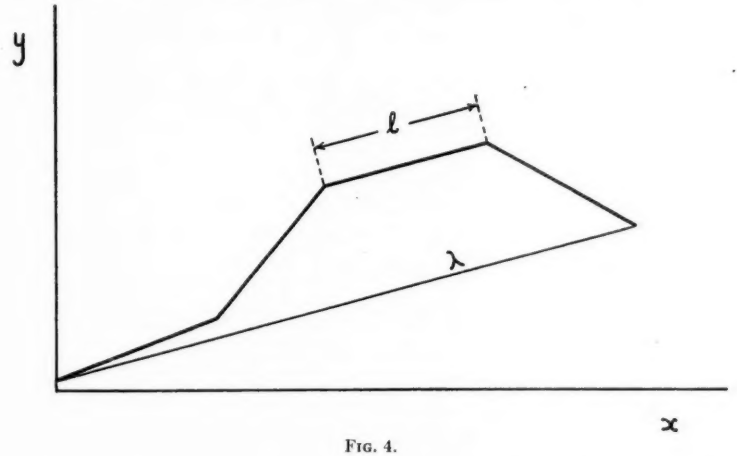

FIG. 4.

Let the coördinates in the plane be described by complex numbers. All vectors making up the chain have a modulus equal to l, and the argument of the vector of link k can be designated by ψ_k. If the k vector is denoted by x_k, the following expression for average square statistical length is obtained:

$$\overline{\lambda^2} = \overline{[x_1 + x_2 + \cdots + x_n][x_1^* + x_2^* + \cdots + x_n^*]}, \tag{2}$$

where $x_k = le^{i\psi_k}$ and the vectors x_k^* represent the complex couple with x_k, *i.e.*,

$$x_k^* = le^{-i\psi_k}$$

Eliminating the brackets:

$$\lambda^2 = l^2[n + \frac{1}{l^2}\sum\sum_{i<k}^{n} (x_i x_k^* + x_i^* x_k)] \tag{3}$$

But each argument ψ_k is made up of a series of consecutively additive small angles of rotation: $\phi_1, \phi_2, \cdots, \phi_n$ and therefore:

$$x_k = le^{i(\phi_1+\phi_2+\cdots+\phi_n)}$$

Hence:

$$x_i x_n^* = l^2 e^{-i(\phi_{i+1}+\phi_{i+2}+\cdots+\phi_k)};$$

and therefore:

$$\frac{\overline{\lambda^2}}{l^2} = n + 2\sum\sum_{i<k}^{n} \overline{\cos(\phi_{i+1} + \phi_{i+2} + \cdots + \phi_k)} \tag{4}$$

$$= n + 2\sum\sum_{i<k}^{n} \overline{\cos\phi_{i+1}\cos\phi_{i+2}\cdots\cos\phi_k}$$

All the other members of the series contain coefficients containing the sines of the angles ϕ_k and, in view of the fact that the latter are equally frequently positive and negative, they fall away.

The angles $\phi_1, \phi_2, \cdots, \phi_n$ are independent of each other, so the average of their product comes down to an averaging of each factor, and

$$\overline{\cos\phi_1} = \overline{\cos\phi_2} = \cdots \overline{\cos\phi_n} = \cos\phi \tag{5}$$

where $\cos\phi$ is the average statistical cosine of the angle of bend of the chain. This angle depends on the forces resisting deformation.

Therefore:

$$\frac{\overline{\lambda^2}}{l^2} = n + 2\sum\sum_{i<k}^{n} \cos^{(k-i)}\phi, \tag{6}$$

After double summation of the progression:

$$\frac{\overline{\lambda^2}}{l^2} = n + \frac{2n\cos\phi}{1-\cos\phi} - \frac{2\cos\phi(1-\cos^{n-2}\phi)}{(1-\cos\phi)^2} \tag{7}$$

If

$$\cos\phi = 1 - \delta \tag{8}$$

the result can be expressed in the following form:

$$\frac{\overline{\lambda^2}}{l^2} = \frac{2n}{\delta} + n + 2\frac{1-\delta-(1-\delta)^{n-1}}{\delta^2} \tag{9}$$

In the present case, as will be seen later, it can be assumed that $n\delta \gg 1$ and, therefore, all terms except the first can be dropped, so finally:

$$\frac{\overline{\lambda^2}}{l^2} = \frac{2n}{\delta} \tag{10}$$

This result is not true of all cases. Thus, for instance, for a small n, *i.e.*, for short chains, it ceases to be applicable.

As will be shown later, at normal temperature, δ is of the order of 1/3. Therefore the assumed approximation is correct for values of n greater than 20–30 units.

Formula (10) is incorrect also when the temperature is very low and δ very small. To get a correct approximation when δ is small and n not too large, so that the product $n\delta$ is still considerably smaller than 1, formula (9) must be divided into a series and only its largest member taken into account:

$$\frac{\overline{\lambda^2}}{l^2} = \frac{2n}{\delta} + n - \frac{2}{\delta} - \frac{2(n-1)}{\delta} + \frac{2(n-1)(n-2)\delta^2}{\delta^2} + \cdots$$

from which:

$$\frac{\overline{\lambda^2}}{l^2} \leqq n^2$$

The physical meaning of this result, which is true for rather low temperatures, or very short chains, is quite clear. It means simply that the chain does practically no bending, and the statistical length of the molecule is equal to its geometrical length.

The opposite extreme case is that of very high temperatures. In this case δ approaches 1, because $\cos\phi$ approaches 0. The statistical length of the chain is given by the formula:

$$\frac{\overline{\lambda^2}}{l^2} = n$$

i.e., this corresponds to free rotation.

In this manner the formula developed in the present work seems to give valid interpretations at both very high and very low temperatures.

For moderate temperatures and reasonably long chains (consisting of at least 20–30 or more links), a sufficient approximation is given by the simple Equation (10). This equation is of the same type as the expression for the motion of a heavy particle possessing active Brownian movement, but tending at the same time to preserve the direction of its original displacement.

III. THREE DIMENSIONAL PROBLEMS

The calculations can be extended to three dimensions, and the average statistical configuration of the chain can be determined. Assume, for example, an organic chain consisting of N links, each of length l, forming with one another a constant angle of 109°, *i.e.*, the normal angle between carbon valences.

Assume that, in this chain, the links are capable of small angular displacements, $\epsilon_1, \epsilon_2, \cdots, \epsilon_N$, provided that the angles between the carbon valences are maintained constant. To investigate the thermal motion of such a chain, make use of the following geometrical construction. Draw all links in space from point O, preserving their original direction. The vectors thus obtained can be designated:

$$\left.\begin{matrix} OA_1, OA_2, OA_3 \cdots OA_n \\ OB_1, OB_2, OB_3 \cdots OB_n \end{matrix}\right\} n = \frac{N}{2}$$

All points $A_1, A_2, A_3, \cdots, B_1, B_2, B_3, \cdots$ will lie on a sphere of radius l.

Note the position of these vectors (Figure 5). The first two, OA_1 and OB_1, can be placed in the plane of the paper. They form an angle of 71° with one another, which is the angle complementing to 180° the angle between carbon valences. Hereafter this angle is referred to as ω.

To find the location of the vector OA_2, a circle with a radius equal to A_1B_1 is drawn around point B on the surface of the sphere. All points lying on the periphery of this circle satisfy the condition that the radius-vectors drawn from the center of the sphere to them form an angle of 71° with the vector OB_1. Point A_2 is located on this periphery in more or less close proximity to point A_1.

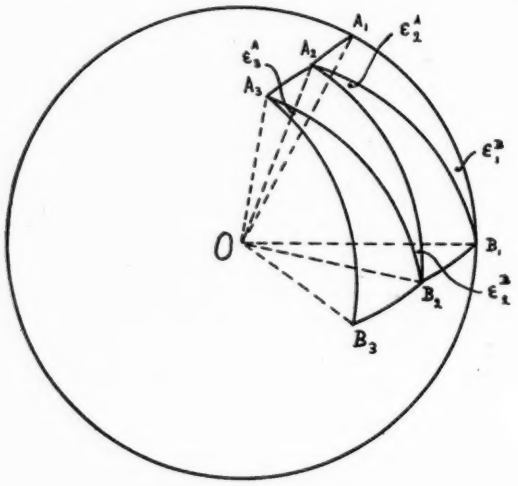

FIG. 5.

The angle between A_1B_1 and B_1A_2 is designated $\epsilon_1{}^B$. This angle characterizes the deviation of the third link from the preceding one. Call the corresponding arc $\xi_{12}{}^A$. In a similar manner, it is possible to locate the position of point B_2, this time by drawing a circle around A_2. This introduces a new angle $\epsilon_A{}^2$ and a corresponding arc $\xi_{12}{}^B$. Continuing this construction to the Nth link a series of vectors characterized by the indices is obtained:

$$\epsilon_1{}^B,\ \xi_{12}{}^A;\quad \epsilon_2{}^B,\ \xi_{23}{}^A\ \cdots$$
$$\epsilon_2{}^A,\ \xi_{12}{}^B;\quad \epsilon_3{}^A,\ \xi_{23}{}^B\ \cdots$$

The indices ξ_i are not independent in nature, and are determined by the angles ϵ_1. Applying spherical trigonometry:

$$\cos \xi_k{}^A{}_{,k+1} = \cos^2 \omega + \sin^2 \omega \cos \epsilon_k{}^B, \tag{11}$$

where ω is, as previously, equal to 71°.

Assuming $\xi_{k,k+1}$ and ϵ_k to be of small magnitude and expanding into a series:

$$1 - \frac{\xi}{2} = 1 - \frac{\epsilon^2}{2} \sin^2 \omega$$

from which it follows that:

$$\xi_{k,k+1} = \epsilon_k \sin \omega \tag{12}$$

Designating further the angles between the rectangular coördinates and the vectors:

$$\begin{array}{ll} OA_1 & \text{by } \theta_1{}^A \phi_1{}^A \psi_1{}^A \\ OB_1 & \text{by } \theta_1{}^B \phi_1{}^B \psi_1{}^B \\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot & \end{array}$$

Designating the statistical square length of the molecule by $\overline{\lambda^2}$, as previously, the length being the distance between the end points of the chain:

$$\frac{\overline{\lambda^2}}{l^2} = \overline{[\cos \theta_1{}^A + \cos \theta_1{}^A + \cos \theta_2{}^A + \cos \theta_2{}^B + \cdots]^2} + \overline{[\cos \phi_1{}^A + \cos \phi_1{}^B \cdots]^2} + \overline{[\cos \psi_1{}^A + \cos \psi_1{}^B + \cdots]^2} \tag{13}$$

To evaluate this sum, the system of triangles on the sphere, constructed by the method described above (Figure 6), must be reviewed. Let the cosines

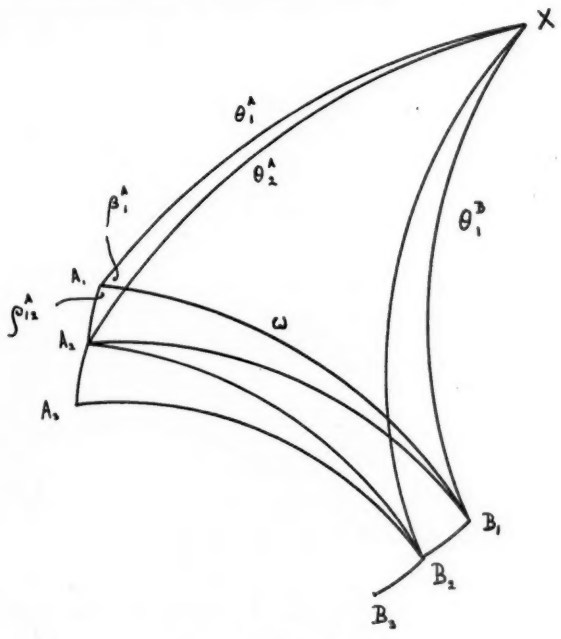

FIG. 6.

of the angles $\theta_2{}^A$, $\theta_2{}^B$, $\theta_3{}^A$, $\theta_3{}^B$, $\cdots$, formed by the vectors OA_2, OA_3, OB_2, OB_3, with the OX axis, be determined.

Assuming the coördinates of the first two links as represented by points A_1 and B_2 to be fixed, the location of the coördinate system are determined. To calculate the coördinates of point A_2, spherical trigonometry must be applied to the triangle XA_1A_2.

$$\cos \theta_2{}^A = \cos \theta_1{}^A \cos \xi_{12}{}^A + \sin \theta_1{}^A \sin \xi_{12}{}^A \cos \alpha_1{}^A \tag{14}$$

where ξ_{12}^A has the same meaning as above, α_1^A is the angle XA_1A_2, formed by arc XA_1 and arc A_1A_2 (XA_1 being numerically equal to θ_1^A, and A_1A_2 equal to ξ_{12}^A. As may be seen from the construction shown in Figure 6.

$$\alpha_1^A = \beta_1^A + \rho_{12}^A,$$

where β_1^A is the angle OA_1B_1, ρ_{12}^A the angle at the base of the isosceles triangle $A_1B_1A_2$. In the same manner, cos θ_3^A is calculated from cos θ_2^A.

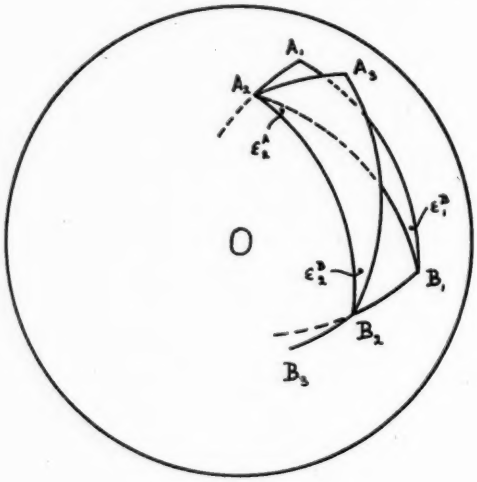

FIG. 7.

Besides the case already considered, there is the alternative whereby the displacement A_2A_3 is in the opposite direction to the first displacement A_1A_2 (Figure 7). It is easy to see that the ideas already expressed are valid for this case also, except for the correction:

$$\alpha_2^A = \beta_2^A - \rho_{23}^A;$$

Combining both cases for the third link:

$$\begin{aligned}\cos\theta_2^A = {} & \cos\theta_2^A \cos\xi_{23}^A + \sin\theta_2^A \sin\xi_{23}^A \cos\rho_{23}^A \cos\beta_2^A \\ & \pm \sin\theta_2^A \sin\xi_{23}^A \sin\rho_{23}^A \sin\beta_2^A \end{aligned} \qquad (15)$$

The right hand side of this equation can be expanded into a series of factors of the small quantity ξ_{32}^A continuing up to members of the order ξ^2. Cos ρ_{23}^A is determined from triangle $A_2B_2A_3$.

From Figure 6 it is evident that:

$$\cos\omega = \cos\omega\cos\xi_{23} + \sin\omega\sin\xi_{23}\cos\rho_{23};$$

from which it follows that:

$$\cos\rho_{23} = \frac{\cos\omega(1-\cos\xi_{23})}{\sin\omega\sin\xi_{23}} \leqq \frac{\xi_{23}\cos\omega}{2\sin\omega} \qquad (16)$$

$$\sin\rho_{23} \leqq 1$$

Substituting in the expression for $\cos \theta_3^A$:

$$\cos \theta_3^A = \cos \theta_2^A \left[1 - \frac{\xi_{23}^{A_2}}{2} \right] + \sin \theta_2^A \frac{\cos \omega}{2 \sin \omega} \cos \beta_2^A \xi_{23}^{A_2} \pm \xi_{23}^A \sin \theta_2^A \sin \beta_2^A \quad (17)$$

Determining β_2^A from triangle XA_2B_2:

$$\cos \beta_2^A = \frac{\cos \theta_2^B - \cos \theta_2^A \cos \omega}{\sin \theta_2^A \sin \omega}; \quad (18)$$

from which:

$$\cos \theta_3^A = \cos \theta_2^A + \frac{\xi_{23}^{A_2}}{2 \sin^2 \omega} [\cos \omega \cos \theta_2^B - \cos \theta_2^A] \pm \xi_{23}^A \sin \theta_2^A \sin \beta_2^A \quad (19)$$

Similarly the symmetrical equation can be expressed in the form:

$$\cos \theta_3^B = \cos \theta_2^B + \frac{\xi_{23}^{B^2}}{2 \sin^2 \omega} [\cos \omega \cos \theta_2^A - \cos \theta_2^B] \pm \xi_{23}^B \sin \theta_2^B \sin \beta_2^B, \quad (20)$$

Since all quantities ξ_{ik} as well as angles ϵ_i, are independent of each other, they must, in order to average them, be replaced by a statistical average expression identical for all angles. Thus for purposes of simplified calculation:

$$\overline{\xi_{ik}^2} = \xi^2.$$

Denote by S_n the sum of directing cosines of a chain containing n links A_i, and an equal number of links B_i:

$$S_n = \sum_{i=1}^{n} (\cos \theta_i^A + \cos \theta_i^B) \quad (22)$$

With the aid of the expression above, the directional cosines of any link by the value of the preceding link can be expressed in all cases. Similarly the expression for a sum of n pairs of links can be replaced by an expression containing the sum of $(n - 1)$ pairs of links:

$$S_n = \cos \theta_1^A + \cos \theta_1^B + \sum_{i=2}^{n} (\cos \theta_i^A + \cos \theta_i^B) \left[1 - \frac{\xi^2(1 - \cos \omega)}{2 \sin^2 \omega} \right] + \xi \sum_{i=2}^{n} (\pm \sin \theta_i^A \sin \beta_i^A \pm \sin \theta_i^B \sin \beta_i^B), \quad (23)$$

or assuming

$$\cos \theta_1^A + \cos \theta_1^B = S_1 \quad (24)$$

$$S_n = S_1 + S_{n-1} \left[1 - \frac{\xi^2(1 - \cos \omega)}{2 \sin^2 \omega} \right] + \xi \sum_{i=1}^{n-1} (\pm \sin \theta_i^A \sin \beta_i^A \pm \sin \theta_i^B \sin \beta_i^B) \quad (25)$$

Taking the statistical average of both parts of this equation, the last sum can simply be dropped, in view of the fact that its components are equally frequently positive and negative and will give zero on the average.

Therefore a recurrent formula connecting the sum of the directional cosines of a chain consisting of n pairs of links with a corresponding sum containing $(n-1)$ pairs of links is finally obtained:

$$\overline{S_n} = S_1 + \left[1 - \frac{\xi^2(1 - \cos\omega)}{2\sin^2\omega} \right] \overline{S_{n-1}} \tag{26}$$

Denoting the expression in the bracket by:

$$\kappa = 1 - \frac{\xi^2}{2(1 + \cos\omega)} \tag{27}$$

and having performed the summation of the geometrical progression, which expresses $\overline{S_n}$, there is finally obtained:

$$\overline{S_n} = S_1 \frac{1 - \kappa^{n-1}}{1 - \kappa} \tag{28}$$

Now proceed to the calculation of $\overline{S_n^2}$

$$S_n^2 = S_1^2 + 2S_1S_{n-1}\kappa + S_{-1}\kappa^2 + \xi^2 \sum_{i=2}^{n} [\sin^2\theta_i^A(1 - \cos^2\beta_i^A) + \sin^2\theta_i^B(1 - \cos^2\beta_i^B) \pm \cdots \tag{29}$$

Again assuming the statistical average of both parts of the equation, and omitting all double sums:

$$\overline{S_n^2} = \overline{S_1^2} + 2S_1\overline{S_{n-1}}\kappa + \overline{S_{n-1}}\kappa^2 + \xi^2 \sum_{i=1}^{n-1} \overline{[\sin^2\theta_i^A(1 - \cos^2\beta_i^A) + \sin^2\theta_i^B(1 - \cos^2\beta_i^B)]} \tag{30}$$

An approximate expression for $\overline{S_n^2}$, valid for the case where all members of the order of ξ^2 by comparison with members of the order of 1 are neglected, is then found. The above expression is then reduced to:

$$\overline{S_n^2} = \overline{S_{n-1}^2} + 2S_1\overline{S_{n-1}} + S_1^2 = S_1^2 + \overline{S_{n-1}^2} + 2S_1^2 \frac{1 - \kappa^{n-1}}{1 - \kappa} \tag{31}$$

This gives:

$$\overline{S_n^2} = nS_1^2 + \sum_{k=1}^{n-1} 2S_1^2 \frac{1 - \kappa^k}{1 - \kappa} = nS_1^2 + 2S_1^2 \left[\frac{n - 1}{1 - \kappa} - \frac{1 - \kappa^{n-1}}{(1 - \kappa)^2} \right]; \tag{32}$$

and approximately:

$$\overline{S_n^2} = \frac{2S_1^2 n}{1 - \kappa} = \frac{4S_1^2 n(1 + \cos\omega)}{\xi^2} \tag{33}$$

Here $n = N/2$ where N is the number of links in the chain. Finally

$$\overline{S_n^2} = \frac{2S_1^2N(1 + \cos\omega)}{\xi^2} \tag{34}$$

With the accuracy of a coefficient of the order of one, the same expression as for the solution in a single plane is obtained if the following substitution is made:

$$\delta = 1 - \cos\epsilon = \frac{\epsilon^2}{2} = \frac{\xi^2}{2\sin^2\omega}$$

In addition, two symmetrical expressions must be added to the calculation of the square length of the chain for the squares of the sums of the directing cosines: ϕ_i and ψ_i. In this case:

$$\lambda^2 = l^2\frac{2N}{\delta(1 - \cos\omega)} \tag{35}$$

In the regions of low or of high temperatures the approximation expressed in Equation (34) is not applicable. The general solution (33) gives the correct answer, even in such limiting cases. All that is necessary is to find other suitable approximations, as was shown in the course of the treatment of the two-dimensional problem.

IV. AVERAGE CHAIN LENGTH IN SOLUTION

It is the object to evaluate quantitatively $\delta = 1 - \cos\epsilon$. Let dn be the number of links in the chain for which the angle ϵ lies between ϵ and $\epsilon + d\epsilon$. Then:

$$\overline{\cos\epsilon} = \frac{\int_0^\pi \cos\epsilon dn}{\int_0^\pi dn}$$

However,

$$dn = n_0e^{-U/kT}\sin\epsilon d\epsilon = n_0e^{-[U_0(1-\cos\epsilon)/2kT]}\sin\epsilon d\epsilon$$

whence:

$$dn = n_0e^{-U_0/2kT}e^{(U_0\cos\epsilon)/2kT}\sin\epsilon d\epsilon$$

On integration we obtain:

$$\overline{\cos\epsilon} = L\left(\frac{U_0}{2kT}\right)$$

where L is Langevin's function:

$$L(x) = \coth x - \frac{1}{x}$$

In the present case, Kistiakowsky and collaborators have shown that: $U_0/kT \geqq 6$, therefore:

$$e^{-U_0/kT} \leqq 2.5 \times 10^{-4}$$

Thus it is sufficiently accurate to write:

$$\delta = 1 - \cos\epsilon = 1 - \left(\frac{1 + e^{-U_0/kT}}{1 - e^{-U_0/kT}} - \frac{2kT}{U_0}\right) \leqq \frac{2kT}{U_0} = \frac{1}{3}$$

Substituting this value of δ in the formula derived above for the statistical length of the molecule:

$$\lambda^2 = l^2 \frac{NU_0}{kT(1 - \cos \omega)}$$

With this formula, several important physical factors can be expressed. First consider the statistical length of a free individual long-chain molecule in solution.

A comparison of the values obtained by Kuhn with the results of the present work is shown in the following table:

n	$\sqrt{\lambda^2}$	$\sqrt{\lambda^2}$ (Kuhn)
16	14	5.7
20	15.5	6.3
100	38	15.5
1000	110	45

From this table it is evident that the molecules of comparatively low-molecular substances (the chain of which contains 15–20 links only, such as fatty acids, soaps, etc.) remain rigid, even in solution. Any deformation caused by thermal motion is insignificant. There is little likelihood of the molecule tangling up into a balllike shape, since such thermal motion as may exist has the character of a torsional vibration of a steel ribbon.

This picture is in full agreement with the views of Staudinger. It can be subjected to direct experimental proof by means of x-ray diffraction. For this purpose solutions of chain molecules having heavy, scattering terminal atoms, *e.g.*, di-iodo or di-bromo derivatives, are used.

Another important deduction from this theory relates to the viscosity of long-chain substances in solution. Staudinger has measured the viscosities of solutions of a large number of substances. These closely agree with the following relation:

$$\lim \left| \left(\frac{\eta}{\eta_0} - 1 \right) \frac{1}{C} \right|_{c \to} = kn,$$

where η is the viscosity of the solution, η_0 is the viscosity of the pure solvent, C is the concentration, n is the number of links in the chain, and k is a constant.

Hydrodynamic considerations show that the left side of this equation should be proportional to λ^2. It must, therefore, be proportional to the molecular weight, *i.e.*, proportional to n. According to the theory of Mark and Kuhn, the coefficient of proportionality is independent of temperature. However, our theory indicates that:

$$k \sim 1/T$$

Unfortunately, this deduction cannot be checked at present in the absence of experimental data over a sufficiently wide range of absolute temperatures.

V. ELASTICITY OF RUBBERLIKE SYSTEMS

Solutions of high-molecular substances, the molecules of which contain many thousands of atoms, behave somewhat differently. There is a substantial difference between the statistical length of a molecule and its geometrical length. Calculations show that this difference is smaller than that which conforms to the theory of Mark and Kuhn. In vulcanized rubber in the solid state, the distance between sulfur bridges is not more than 100 to 300 l. Since

only these parts of the chain are free to move, the importance of the Brownian movement in the molecules is greatly diminished. But even if vulcanization is ignored, and, as Kuhn did, the problem is confined to single independent and very long rubber chains, it can be shown that the theory of kinetic elasticity of Mark and Kuhn is inadequate to account for elastic forces of the magnitude observed in practice.

Let the Brownian movement of a chain which is being stretched by external forces be examined, and let it be assumed that elasticity is caused only by thermal motion. The calculation can be simplified by using the formulas derived from the theory of Brownian motion. The space configuration of the chain can be regarded as the path of a heavy particle during the process of diffusion. This particle has a tendency to preserve the direction of its original velocity vector while colliding with particles of gas. From the theory of Brownian motion:

$$\overline{\Delta^2} = 2D\tau$$

where Δ is the displacement of the particle in any given direction, D is the coefficient of diffusion and τ is the interval of time. Since, in our diffusion model, $\overline{\Delta^2}$ is only the average square length of the molecule $\overline{\lambda^2}$, we can find an expression for $D\tau$ (coefficient of diffusion $\times$ time) by means of the equation:

$$\overline{\lambda^2} = \frac{2}{1 - \cos\omega}\frac{l^2 n}{\delta} = 2D\tau,$$

whence

$$D\tau = \frac{l^2 n}{\delta(1 - \cos\omega)}$$

Smoluchovsky's equation for the diffusion of a Brownian particle under the action of a force f is:

$$\bar{\Delta} = \gamma f \tau,$$

where Δ is the displacement in the direction of the force f, τ is the time, and γ is a coefficient expressing the mobility.

With the help of the formula:

$$D/\gamma = kT$$

the above relation can be rewritten as follows:

$$\bar{\Delta} = \frac{D\tau f}{kT}$$

Substituting for $D\tau$, this expression becomes:

$$\bar{\Delta} = \frac{l^2 n f}{kT\delta(1 - \cos\omega)}$$

From this the following equation for the modulus of elasticity E is obtained:

$$E = \frac{f}{\Delta}\frac{\delta kT(1 - \cos\omega)}{nl^2} = \frac{1}{nl^2}\frac{2(1 - \cos\omega)}{U}k^2T^2$$

Comparing this with the formula obtained by Mark and Kuhn:

$$E = \frac{3kT}{nl^2} \frac{1 - \cos \omega}{1 + \cos \omega},$$

it is evident that the calculation of elastic forces in the chain results in a twenty-fold lowering of the absolute value of the elasticity modulus. For this reason the agreement which Kuhn found between the orders of the measured and calculated values for Young's modulus must be regarded as fortuitous. The value of the modulus E as corrected in the present work is of a lower order than the experimental value. It must, therefore, be concluded that the picture of "kinetic elasticity" originating in the thermal motion of the particles is inadequate to account for the real elastic forces in rubber.

It should be noted, further, that the modulus of "kinetic elasticity" varies with the square of the absolute temperature, and not linearly, as deduced from Mark and Kuhn's theory.

The analogy with diffusion which has been used here is no longer justifiable in regions of low temperature, where kT is so small that the chains remain practically straight, which renders the basic Equation (35) incorrect, as has been shown above. In this case the concept of kinetic elasticity apparently loses its significance, and can be entirely rejected.

For regions of high temperature, a different approximation for λ^2 must be used. However, the diffusion theory remains valid, and leads to the same solution given by Kuhn and Mark.

The extraordinary elastic behavior of rubber cannot be explained by a consideration of the thermal motion of individual isolated molecules. To develop a correct theory, it is essential to take into consideration the interaction of the particles and the change in free energy due to displacements of their centers of gravity. This must not be done in the nature of a correction, but must be made one of the fundamental factors in the process of deformation.

SUMMARY

1. The theory of Mark and Kuhn, which assumes full freedom of rotation around the bonds of an organic chain, is criticized. Objections are raised as to the mechanism of elasticity of rubber proposed by these two investigators.

2. Based on the findings of Kistiakowsky, Pitzer and others, calculations are made of the elastic forces which hamper free rotation and thereby bring about a ribbonlike structure of the molecule. Calculations show the effect of these elastic forces on the thermal motion of the molecules and on their shape in solution.

3. It is shown that, if care is taken to calculate the modulus of elasticity correctly, the dynamic elasticity assumed by Mark and Kuhn is inadequate to explain the elastic behavior of rubber.

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THE COURSE OF AUTOÖXIDATION REACTIONS IN POLYISOPRENES AND ALLIED COMPOUNDS

I. THE STRUCTURE AND REACTIVE TENDENCIES OF THE PEROXIDES OF SIMPLE OLEFINS *

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The structural changes which occur in olefinic substances when they undergo oxidation by molecular oxygen have never been elucidated, although many of these changes, such as the autoöxidation of drying oils and of rubber, are of enormous practical importance. It has commonly been supposed that absorption of molecular oxygen occurs at some or all of the ethylenic centers to give peroxidic groupings, which, for want of a better representation and following Engler's suggestion[1], have been formulated as cyclic structures: $\begin{matrix} C & - & C \\ | & & | \\ O & - & O \end{matrix}$. There is, however, little direct evidence supporting such a formulation beyond (1) that the unsaturation of the autoöxidized substance usually decreases progressively (although not in quantitative correspondence) as oxygen-intake increases, and (2) that frequently the reaction ends in hydroxylation of the double bond to yield a 1,2-glycol, or in complete scission of the carbon chain at the double bond. The peroxidic groupings, as is well attested, show a tendency to decay, with formation from the peroxidized olefin of one or more of a wide variety of oxygenated materials, including olefin oxides, ketones, glycols, ketols, miscellaneous oxygenated compounds of unknown structure (but important in the drying oils, since they seem to be largely responsible for the formation of films and skins), and, as the result of chain-scission, aldehydes, ketones, carboxylic acids, and hydroxycarboxylic acids. If it is assumed that all these types of product, as well as certain simple degradation products such as water, carbon dioxide, and the lower fatty acids, arise from simple peroxides of the original olefins, it becomes difficult on the basis of present information to fit them into a coherent scheme and to reconcile many apparently discordant observations.

In attempting to devise such a scheme, consideration must necessarily be given to the effect on the course of reaction in the somewhat varied ways in which the autoöxidations can be promoted and the conditions under which they are conducted. The most important influences seem to be catalytic agents or agencies and the temperature conditions. Many different organic, inorganic, and metallic catalysts, as well as light of different wave-lengths, have been used to initiate and facilitate autoöxidation, and it is to be noted that the manner of their application may have important effects on the final products; also, raising the temperature above room temperature is recognized generally to accelerate reaction. Whether either catalytic influences or the

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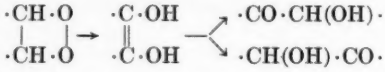
conditions of reaction can ever influence the character of the primary oxidation reactions (as distinct from controlling the purely secondary autoöxidative changes), however, is not known with certainty. In most autoöxidation reactions, it is fairly clear that reaction begins with the absorption of oxygen and the immediate production of peroxide groups; in other reactions the participation of peroxides is not so obvious (since no peroxides survive), but is commonly accepted as a primary feature of the reaction mechanism. A contrary view is, however, still sometimes expressed, and fairly recently Szent-Györgyi[2] concluded that by the influence of a specific type of chemical catalyst the absorption of oxygen can lead directly, without intervention of peroxides, to the formation of olefin oxides.

The view that autoöxidation occurring at olefinic centers leads first to the formation of cyclic peroxide groups, then to that of oxido groups, and later to glycols or products of chain scission, has often been expressed, although it could not be established as a general course of reaction in view of innumerable observations to the contrary. Ellis[3] obtained yields of crystalline oxido compounds as high as 15 per cent from elaidic and oleic acids, as well as considerable yields of obviously chain-scission products. An alternative, however, to the cyclic peroxide–oxide–glycol–scission product sequence has been postulated by Willstätter and Sonnenfeld[4], which seems to be accepted by most recent writers on the autoöxidative changes occurring in vegetable oils[5]. This holds that the cyclic peroxide groups formed in the first stage of oxidation have the ability to isomerize to the corresponding unsaturated diol or its tautomeric ketol:

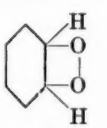


and would mean, if it were correct, that there is a direct and very simple path connecting the initial formation of a peroxide group with the final occurrence of chain scission at the original double bond, since the unsaturated enol might well be deemed to be susceptible to further oxidative attack culminating in scission. The hypothesis, however, fails completely to make any provision for the undoubted formation in some autoöxidations of oxido compounds and saturated 1,2-glycols, or indeed for the occurrence of secondary autoöxidative change at all in peroxides derived from the substituted system: $\cdot CR : CR' \cdot$ (R, R′ = alkyl), since such peroxides would be structurally incapable of giving ketol tautomerides. It is the object of this and subsequent papers to examine various aspects of the autoöxidation problem as it affects simple and high-molecular unconjugated olefinic substances[6] with a view to trace the main and subsidiary changes and to correlate these with certain other types of oxidative reaction to which olefinic substances are susceptible.

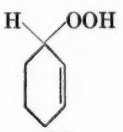
In 1928 Stephens[7] discovered that cyclohexene, when treated with oxygen in daylight, gave a liquid peroxide, $C_6H_{10}O_2$, presumed to be a double-bond adduct (I), which could be isolated by distillation. In 1936 one of us (with E. S. Narracott), in the course of preliminary experiments on the oxidation of rubber, found that when commercial xylene was used as solvent and an organic cobalt salt as catalyst, the xylene underwent slow oxidation with production of tolualdehyde, *m*- and *p*-toluic acid, and an alcohol which was doubtless toluic alcohol. This was one of a number of interesting examples, which it is hoped to discuss later elsewhere, of the strong reactivity of methylene groups situated in the α-position to olefinic double bonds—a reactivity involving

replacement or separation of hydrogen atoms. On the assumption that the formation of a peroxide group is the first step in the oxidation by molecular oxygen, the primary oxidation product of xylene must have been a hydroperoxide, $CH_3C_6H_4CH_2OOH$, comparable with Rieche's monoalkyl peroxides, and it was of great significance, as reflecting the relative natural tendencies towards displacement of olefinic and methylenic hydrogen atoms in the system $\cdot CH : CH \cdot CH_2 \cdot$ (at least in certain types of reactivity), that in xylene the usual aromatic replaceability of nuclear hydrogen is actually superseded by replaceability of α-methylenic hydrogen atoms. α-Methylenic reactivity, as distinct from ordinary double-bond additivity, appears indeed to be potentially important in the chemistry of most monoölefinic and unconjugated polyolefinic compounds, and especially is this true of the latter, since in many of these, owing to the multiple unsaturation, the mobility of α-methylenic hydrogen seems to be enhanced.

Stephens's peroxide was reëxamined by Hock and Schräder[8], who obtained certain interesting results as regards the reactivity of the peroxide (see below) but agreed with Stephens's formulation of the peroxide as the double-bond adduct (I). Our own examination of cyclohexene peroxide, begun in 1939 with the object of throwing light on a number of perplexing observations made over several years of study of the autoöxidation and general reactivity of rubber, was forestalled in an important respect by Criegee, Pilz, and Flygare[9], who showed that the peroxide formed from cyclohexene in ultraviolet light must be a hydroperoxide (II) still containing a double bond, since (1) it is reducible by sodium sulfite to cyclohexen-3-ol (III), (2) it absorbs 1 mol of bromine per mol, and (3) it contains one atom of active hydrogen per mol.



(I)



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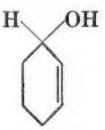


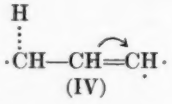
(III)

This confirmed the above-mentioned indications of the importance of α-methylenic reactivity in the chemistry of olefinic systems, and rendered desirable further investigation, especially of the secondary autoöxidation processes, of cyclohexene and other allied olefins.

POINT OF OXIDATIVE ATTACK

In numerous oxidations of carefully purified cyclohexene, carried out by us in quartz flasks in the radiation from a mercury-vapor lamp, there was usually formed in 2–4 hours, at temperatures between 30° and 40°, about 30–40 per cent of oxygenated material containing about 80 per cent of monomeric peroxide, as determined both by direct estimation of peroxidic oxygen and by isolation of the pure peroxide by fractional distillation at greatly reduced pressure. The peroxide thus isolated behaved exactly as described by Criegee in regard to unsaturation, active hydrogen content, and reducibility to cyclohexenol, and also was quantitatively reducible by hydrogen and platinum to crystallizable cyclohexanol, and not to cyclohexane-1,2-diol. Hence, peroxide formation in itself involved none of the reduction of unsaturation which must result from any addition of oxygen to the original double bond; on the contrary, oxidative attack was here confirmed to affect in the primary

reaction only the α-methylene groups. The mode of attack, involving displacement of a methylenic hydrogen atom, is doubtless similar to that occurring in the peroxidation of saturated hydrocarbons, although the process is enormously facilitated in olefinic substances by an enhanced tendency to dissociation of hydrogen promoted apparently (in spite of the fact that the dissociation is probably of free-radical rather than of ionic character) by normal electronic displacements in the double-bonded system (IV); furthermore the attack is found to be accelerated, as might perhaps be expected, if an inductively-acting alkyl group is attached to the ethylenic carbon atom adjacent to the methylene group (system V), as occurring in trimethylethylene or 1-methylcyclohexene, In the general case, therefore, although any α-methyl-



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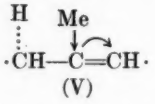
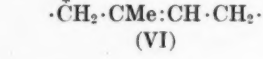


(V)

ene group is a potential reactive center, the most likely point of attack where several such groups are present may be expected to be that one in which the tendency to dissociation of hydrogen will be most facilitated by normal electronic polarization. Hence, although attack is possible at either of the methylene groups in the unsubstituted system $\cdot CH_2 \cdot CH : CH \cdot CH_2 \cdot$, it is most likely to occur to the greatest extent at the points distinguished by asterisks in the systems (VI–X)[10].



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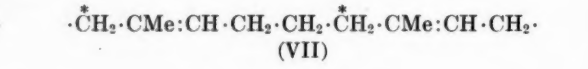

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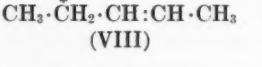

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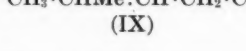

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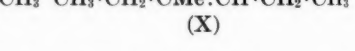


(X)

Peroxide decomposition.—Organic peroxides have very different degrees of stability, as is well seen in their widely-varied ease of reduction and their stability at room temperature. It is well attested that the secondary reactions following the initial formation of peroxide groups commonly involve some loss of unsaturation, and a review of numerous published observations makes it clear that the rapidity of this loss varies with the character (stability or reactivity) of the peroxidic substances formed, and with the experimental conditions. Both of these factors affecting the ease of peroxide decay are very important. In the case of cyclohexene, as seen above, a few hours' autoöxidation under the most favorable conditions gives oxygenated material which contains much pure hydroperoxide but, even so, the original olefinic unsaturation of the hydrocarbon (per molecule) does not survive in the product wholly undiminished. The same holds good in the case of two other autoöxidations which we have studied, *viz.*, those of 1-methyl- and 1,2-dimethyl-cyclohexene. If, however, in these examples the temperature during oxidation is allowed to rise above 40°, or the peroxide is formed so slowly, *e.g.*, without catalysis by light or other agency, that the oxidation process is unduly prolonged, *e.g.*, for many days, the yield of pure peroxide becomes much diminished and that of secondary products correspondingly increased. Other substances are similar to cyclohexenes in this respect. Rubber when oxidized rapidly in solution under good illumination at about 15° incorporates 80 per cent of the oxygen

in peroxide form during the early stages of reaction, although later this high yield decreases; but if the oxidation is conducted under less favorable conditions no high percentage of the oxygen intake survives as peroxide at any stage, and in commercial processes, where an organic cobalt salt is used as catalyst and the temperature is allowed to rise unchecked, only traces of peroxide survive. With autoöxidized linseed oil, many previous observations indicate that the peroxide content rises during the first few hours to a maximum which represents only a fraction of the total oxygen intake (25–40 per cent according to the experimental conditions), and afterwards slowly decreases; at the same time the unsaturation decreases.

The fact that the increase in the oxygen uptake (with concomitant formation of peroxidic substances) is accompanied by a decrease in unsaturation has usually been interpreted to mean that oxygen adds directly in peroxide form at the double bonds, although the gross inexactitude of the quantitative relationship between the two has been a continual source of perplexity. Scrutiny of the wealth of recorded data on autoöxidative changes leaves little doubt but that the diminution in unsaturation, whether this is slow or rapid, is partly a matter of the experimental conditions. This is understandable if the primary reaction, *i.e.*, the absorption of oxygen to form peroxide groups, is recognized to consist generally in the formation of hydroperoxide groups on the α-methylenic carbon atoms, for then the actual oxygen absorption does not affect at all the unsaturation of the system; only later, when the secondary reactions brought into being by the decay of peroxide groups begin, does the unsaturation become affected, and the prevailing conditions of reaction are likely to influence materially the speed of decay and hence the length of life of the peroxide groups and probably to affect the mode of their decomposition. The secondary reactions tend almost entirely towards saturation of the olefinic centers (unless conditions which promote dehydration of the secondary products are employed), and hence the ultimate autoöxidation products will often contain but little peroxide and be almost saturated: the actual peroxide content and the condition of unsaturation at intermediate points will depend mainly on the respective rates of formation and decomposition of the peroxide. What these reactions are, and the way in which their course and progress are affected by the experimental conditions, is shown in part below.

As noted by Criegee, the peroxide of cyclohexene which is formed in a few hours under good illumination at about 30° is much purer than Hock's original product, formed during a long period (200 hours) in diffused light. But even the best products, in spite of being distilled expeditiously at pressures below 1 mm. (bath temperature below 80°), give a small peroxide fraction, of rather low peroxide content and slightly high boiling point, in which some degree of secondary change has occurred; any elaborate fractionation of the peroxide unless by molecular distillation at low temperatures serves only to increase this fraction. We have found also that, even under the most favorable conditions of operation, the oxidation product does not consist of unchanged cyclohexene and the hydroperoxide fraction only. Careful fractionation of the lower-boiling portion of the product at reduced pressure always gives some cyclohexene oxide and some cyclohexenol in addition to the unchanged cyclohexene; and if this fractionation is conducted at atmospheric pressure, some of the cyclohexenol is dehydrated, and the water so liberated hydrates a part of the cyclohexene oxide to *trans*-cyclohexanediol, m.p. 104°. That the oxide and cyclohexenol are formed during the oxidation, and not subsequently, can be demonstrated by reducing the oxidation product with sodium sulfite imme-

diately the oxygen intake ceases, and then fractionating the peroxide-free mixture. It is difficult to envisage any likely means of formation of the simple olefin oxide, *e.g.*, by hydrolysis or reduction of, or by loss of free oxygen from, the peroxide, under the conditions of reaction employed other than the direct oxidation of cyclohexene by the cyclohexene peroxide. This would be analogous to the oxidation of olefins to oxido derivatives by peracids, such as perbenzoic acid, and might be represented as being initiated by the occurrence of coördination between a polarized ethylenic carbon and a peroxidic oxygen atom, and completed by the elimination of a molecule of alcohol (cyclohexenol) from the coördination complex:

$$\cdot CH{:}CH\cdot + R\cdot OOH \rightarrow \cdot CH(HO^{+}\cdot OR)\cdot CH\cdot \rightarrow \cdot CH\cdot CH(O)\cdot + R\cdot OH \qquad (A)$$

It is important to note that the formation of cyclohexene oxide in this way must necessarily involve a bimolecular reaction, and it was of interest to discover whether, by heating together the suggested reactants, cyclohexene oxide is produced. Tests of this kind carried out at 100° gave cyclohexene oxide in small yield, together with cyclohexenol[11] and some polymeric material. It is readily understood why no large yield of oxido compound is formed, since the latter is likely to react at 100° (especially in the presence of small amounts of acid)[12] with the hydroxylic compounds present. The rapid autoöxidation of 1-methyl- and of 1,2-dimethyl-cyclohexene at 30–40° in ultraviolet light was also found to give rise to the corresponding oxides (1-methyl- and 1,2-dimethylcyclohexene 1,2-epoxide) and alcohols (1-methylcyclohexenol and 1,2-dimethylcyclohexen-3-ol), in about equal amounts, as well as to a good yield of the parent hydroperoxides; here, however, the low-boiling decomposition products were produced in rather larger yield. The oxides gave on hydrolysis with water at 110°, or better with dilute sulfuric acid, the high-melting forms (respectively) of 1-methyl- and 1,2-dimethylcyclohexane-1 : 2-diol. The alcohol from the peroxide of 1-methylcyclohexene proved to be a mixture of the 6- and the 3-hydroxy compound, the former preponderating, so the peroxide, in conformity with the views on the point of oxidative attack expressed above, contained both the 6- and the 3-hydroperoxide. This fact received confirmation in several ways.

Ketone formation.—As seen above, one of the decomposition products of cyclohexene hydroperoxide is cyclohexene-3-ol, and it is a striking fact, noted by Schmidt[13], that in various autoöxidations of cyclic olefins described in the literature, similar unsaturated alcohols have almost invariably been obtained. A review of the examples shows that the hydroxy group is attached to that one of the ring carbon atoms at which, in our view, hydroperoxidation would be most likely to occur, except that in the case of α-pinene, in which the system $\cdot CH_2\cdot CH{:}CMe\cdot CH\langle{}^{C}_{C}$ occurs, attack at both (alternatively) of the α-carbon atoms has been observed. These autoöxidations have been carried out at 70° or above, or for long periods at a lower temperature, usually in presence of a catalyst. In many of the examples, *e.g.*, see Table I, the alcohol is accompanied by the corresponding ketone, and it seems at first sight not unlikely, especially in view of the fact that water is almost invariably formed in olefinic autoöxidations, that direct dehydration of the olefinic hydroperoxide to form

TABLE I

Olefin	Catalyst	Temperature	Time	Ketone	Authors
Cyclohexene	Os (colloidal)	?	22 hours	Cyclohexan-1-ol-2-one	Willstätter and Sonnenfeld[14]
1-Methyl-cyclohexene	None	95°	?	1-Methylcyclohexen-6-one	Dupont[15]
"	Fe phthalocyanine	70°	72 hours	"	Cook[16]
1,2-Dimethyl-cyclohexene	None	70°	1 week	1,2-Dimethylcyclohexen-3-one	Dupont[17]
α-Pinene	None (iron vessel)	Room temp.	6 months	Verbenone	Blumann and Zeitschel[18]
"	Fe phthalocyanine	70°	4 days	"	Cook[16]
"	Os; sunlight	?	?	"	Wienhaus and Schumm[19]
β-Pinene	Co resinate	*ca.* 30°	88 hours	Pinocarvone	Schmidt[13]
Limonene	None	Room temp.	2½ months	Carvone	Blumann and Zeitschel[20]
Tetralin	Fe phthalocyanine	70°	12 hours	α-Tetralone	Cook[16]

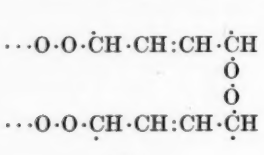
a ketone may have occurred:

$$\cdot CH(OOH)\cdot CH{:}CH\cdot \rightarrow \cdot C(=O)\cdot CH{:}CH\cdot + H_2O \qquad (B)$$

But in none of our autoöxidation experiments at 30–40° with cyclohexene or the more rapidly autoöxidizable 1-methyl- and 1,2-dimethyl-cyclohexene has any recognizable amount of cyclic ketone been formed, although water is a product of reaction. Also, it is plain that to the extent that a hydroperoxide, R·OOH, undergoes dehydration, to that extent it relinquishes its oxidative habit, which much evidence shows to be the principal reactive tendency; furthermore, there is little in the literature to indicate that alkyl peroxides may be able to undergo dehydration, unless the ordinary decomposition of hydrogen peroxide to water and oxygen is accepted as an indication. Nevertheless, both Cook[16] and Dupont[21] have reported the formation in diffused light at 70° and 90°, respectively, of a cyclic ketone from 1-methylcyclohexene[22], the former author using an active iron catalyst and the latter none at all. It is clear that, whereas the alcohol appears to be a necessary primary decomposition product of the peroxide, the ketone does not; also it appears that, for the production of the ketone in appreciable amount, either a higher temperature than 40° is required, or some other condition (probably one involving the activity of the catalyst) needs to be fulfilled. We have not succeeded in directly oxidizing cyclohexen-3-ol to the corresponding ketone by exposing it to oxygen in ultraviolet light at 30–40°, neither the oxygen nor the organic peroxides which are readily formed from the alcohol under these conditions having apparently the necessary oxidative power. This suggested, although it in no way proved, that the ketone is formed directly from the peroxide, rather than indirectly *via* the alcohol. Hence it seemed most reasonable to look for the origin of the ketone in the isomerizing capacity or in one of the paths of direct decomposition of the hydroperoxides.

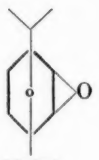
Ketone formation by isomerization of the peroxides or oxides.—The autoxidation of conjugated diolefins appears to yield either polymolecular peroxides in which the diene units are terminally linked as in (XI)[22] or unimolecular ones such as ascaridol (terpinene peroxide) and the peroxides of 2 : 4-cholestadiene, ergosterol, dehydroergosterol, rubrene, naphthacene, pentacene, anthracene, etc. In all of these unimolecular examples the existing evidence leaves little doubt as to the formation of the peroxides by the transannular addition of oxygen at the ends of conjugated diene systems[23]. Now in the case of ascaridol (XII) it has been shown that the transannular peroxide passes, on heating at

150°, into the oxide (XIII), while the peroxide formed from 2,4-cholestadiene under mild illumination isomerizes (in alcohol solution) on exposure to sunlight to give a saturated ketone. The same ketone is formed directly from the cholestadiene if oxygenation takes place in sunlight, and Skau and Bergmann[24]



(XI)

(XII)



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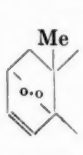
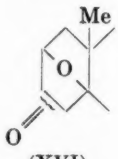


(XIV)

(XV)



(XVI)

suggest that the peroxide (XIV) isomerizes first to the oxide (XV), which immediately rearranges to give the ketone (XVI); the location of the carbonyl group, however, at position 3 or 4 in (XVI) has not yet been precisely determined. Ergosterol peroxide can also be converted into an epoxide-ketone, but in this case by heating at 185–190°[25] the ketone group has not been shown to appear in the bridged ring, and indeed it may well occur at an original center of unsaturation in the side chain[26].

Among recorded investigations of the autoöxidation of unconjugated olefinic substances there is, so far as we are aware, no clear instance where direct isomerization of peroxide to ketone (similar to the foregoing examples in the conjugated series) has been demonstrated. The analogous change in the unconjugated olefin series to that represented by the transformation (XIV) → (XV) → (XVI) would be:

$$>C(OOH)\cdot CH{:}CH\cdot \rightarrow >C(OH)\cdot \underset{\diagdown O \diagup}{CH\cdot CH}\cdot \rightarrow >C(OH)\cdot CO\cdot CH_2\cdot$$

or

$$>C(OH)\cdot CH_2\cdot CO\cdot$$

Morrell and his collaborators[27] have claimed that enolizable α-ketols are normally formed in the case of autoöxidized drying-oil acids or glycerides in the manner: $\begin{matrix}\cdot CH\cdot CH\cdot \\ | \quad | \\ O\text{—}O\end{matrix} \rightarrow \begin{matrix}\cdot CH\cdot CO\cdot \\ | \\ OH\end{matrix}$, but we can find no justification of the claim in any of the experimental evidence which these authors advance; and, indeed, the measurement of ketol content in terms of carbonyl and active hydrogen content by these and other authors[28] is necessarily rendered invalid by the fact that the peroxide groups present are highly oxidative, hydroxylic ·OOH groups, and not the less reactive, nonhydroxylic ·O·O· groups assumed by them. In numerous autoöxidations of cyclohexene and 1-methylcyclohexene, we have found none of the easily recognizable α-ketol among the oxidation products, although Willstätter and Sonnenfeld[4], as noted above, obtained some α-ketol (cyclohexan-1-ol-2-one) under their conditions of autoöxidation. In view,

however, of the frequent formation of α-ketols as intermediates during the oxidative scission of double bonds, *e.g.*, by permanganate, this product seems most likely to have been derived by the further oxidation of the corresponding epoxide or saturated 1,2-diol. At present, therefore, the occurrence of a substantial degree of ketone formation by an isomerization of peroxide groups analogous to that reported for conjugated compounds seems doubtful, but it is hoped to publish further observations on this point later.

Ketone formation by peroxide decomposition.—Various authors have referred to the dual role of autoöxidation catalysts in promoting both peroxidation and the subsequent decomposition of the peroxides, although the balance between formation and decomposition does not appear to have been studied. Cook[16] obtained methyl cyclohexenone by autoöxidation of methylcyclohexene at 70°, using ferrous phthalocyanine as catalyst, but in our experiments no significant amount of ketone was formed by oxidation in ultraviolet light at *ca.* 35°. We have, therefore, tested the ketone-forming action of Cook's catalyst on pure methylcyclohexene hydroperoxide, and found that this catalyst promotes a very energetic decomposition of the peroxide to cyclic alcohol, cyclic ketone, and other products, the ketone being in substantial yield and consisting of two isomeric compounds, 1-methylcyclohexen-6- and -3-one. Of these isomerides the former preponderated, so it is fairly certain that they are derived directly from the corresponding alcohols or the parent hydroperoxides. In the case of cyclohexene hydroperoxide, ferrous phthalocyanine caused similar energetic decomposition, with formation of much cyclohexenol, a substantial yield of ketone, a little cyclopentene-1-aldehyde, and other products. The ketone was cyclohexene-3-one, and the aldehyde a scission product formed by causes discussed later. Similarly, decomposition of 1,2-dimethylcyclohexene hydroperoxide gave a substantial yield of 1,2-dimethylcyclohexen-3-one, together with the related cyclic alcohol and other products. The ketone was contaminated with a little of a second ketone, which appeared to be the ring-scission product, 1,4-diacetylbutane.

As regards the identity of the immediate precursor of the ketonic products (hydroperoxide or alcohol) in these catalytic decompositions, the evidence is not yet clear. Water is always eliminated in the decompositions, as though by dehydration of the hydroperoxide (Equation B), but so it is in autoöxidations in which no ketonic product is formed. The normal decomposition product of the peroxide always appears to be the cyclic alcohol and, to permit the formation of this substance, the potential oxidizing power of the active peroxide groups must be dissipated. This oxidizing capacity is largely utilized in oxidative attack, culminating in chain scission, at the unsaturated centers, but it may well be that in the presence of an active catalyst it is sufficiently energetic to bring about oxidation of the cyclic alcohol to the corresponding ketone. A crucial test on this point remains to be applied. It is of interest, however, to note that the ketones formed in this way by catalytically-promoted peroxide decomposition, unlike those which would be formed by peroxide isomerization, are unsaturated, whereas the trend of autoöxidation in vegetable oils seems, according to published observations, to be towards the production of complete saturation. Possibly the formation of unsaturated ketones is mainly a special characteristic of hydroaromatic autoöxidations.

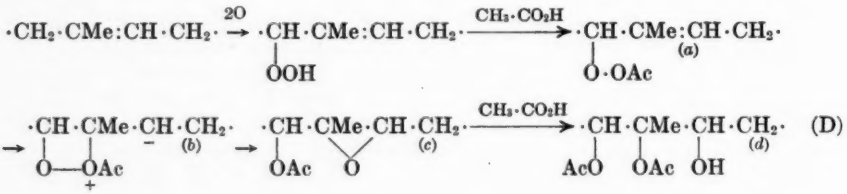
Vigorous decomposition of cyclohexene hydroperoxide occurs when it is heated to about 120° in an open vessel. The reaction is probably similar to that promoted by ferrous phthalocyanine, but the products have not been closely examined.

Oxidative action of hydroperoxides in the presence of acids.—One of us, with Bloomfield[29], observed that the oxidation of rubber, when carried out in presence of a cobalt catalyst, is greatly accelerated if a little acetic anhydride is added; moreover, the action of the acetic anhydride is not simply catalytic, since the oxidation products are extensively acetylated. Later, one of us noticed that when small lumps of rubber are refluxed for a day with acetic anhydride, little except slight swelling of the rubber ensues, but when the anhydride is refluxed rapidly over the rubber in an open extraction tube, the hydrocarbon undergoes rapid and advanced degradation, in which atmospheric oxidation is the principal factor. The influence of acids does not appear to be confined to organic acids, since attempts to hydrate dihydromyrcene, $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_3$, by refluxing it with sulfuric acid in an open vessel (with a little silver sulfate as hydration catalyst) gave oxidation products instead of hydration products. On the other hand, alkali has no marked promoting action on the autoöxidation of rubber, although pyridine appears to assist reaction.

The reactive hydroperoxides which are formed under nearly anhydrous conditions by the action of oxygen on olefins would be expected to react immediately with organic acids to give alphyl esters of the corresponding peracids:

$$R{\cdot}OOH + R'{\cdot}CO_2H \rightarrow R'{\cdot}C(OH)_2{\cdot}OOR \rightarrow R'{\cdot}CO{\cdot}OOR + H_2O \qquad (C)$$

which in turn would behave like free peracids in their additivity to olefinic centers:

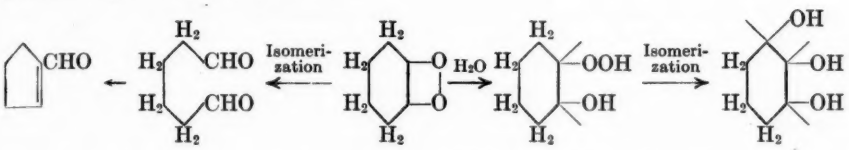


(D)

The epoxide shown in stage (*c*) probably never appears as an isolable compound; also the addition of acetic acid at the epoxy group (change $c \rightarrow d$), and of ·OAc at the double bond (change $a \rightarrow b$), may take place in the reverse direction to that shown in scheme (D). The reaction in presence of an acid anhydride would be precisely analogous, yielding eventually for pure acetic anhydride (free from acetic acid) triacetoxy derivatives, $\cdot CH(OAc){\cdot}CMe(OAc){\cdot}CH(OAc){\cdot}CH_2\cdot$; but with either the free fatty acid or the anhydride, further oxidative attack might lead to scission between either pair of oxygenated carbon atoms, although this probably would not occur nearly so readily with esterified polyalcohols as with the corresponding free alcohols. The satisfactory confirmation of such a course of reaction in the case of rubber has only recently become possible by the development in connection with this work of a precision method for the determination of active hydrogen in high-molecular substances[30]. The details of this confirmation form the subject of Part III.

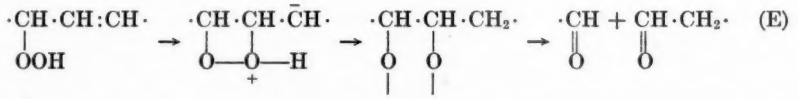
Whether or not in the above-cited oxidation of dihydromyrcene in presence of dilute sulfuric acid, there is slow and transient formation of peracid (? permonosulfuric acid), there is certainly engendered a vigorous peroxidic oxidizing capacity when pure cyclohexene- and alkylcyclohexene hydroperoxides are

mixed with dilute sulfuric acid. Hock[31] observed that cyclohexene peroxide, when allowed to stand with sulfuric acid at 35–40°, gave mainly cyclopentenealdehyde (about 20% yield) and cyclohexane-1,2,3-triol (50% yield)[32], and he sought to explain their formation from a supposed cyclic type of peroxide by postulating two isomerizations:



Now the triol is precisely the product which would be expected to arise in accordance with the foregoing schemes (C) and (D) if an aqueous mineral acid were substituted for the organic acid or anhydride, but the formation of cyclopentenealdehyde, *i.e.*, the dehydrated aldol from adipic dialdehyde, is more difficult to formulate, since the oxygeno-substituent has apparently disappeared from the α-carbon atom. It seemed possible at first that the parent adipic dialdehyde might have arisen by the action of the hydroperoxide, and subsequently perhaps of peracid, on residual cyclohexene in the peroxide employed (Equation A), but many repetitions of Hock's experiment with peroxide which had been entirely freed from cyclohexene have always given some cyclopentenealdehyde, together with a little cyclohexenol, although the main products were cyclohexanetriol and a "dimeric" acidic residue; moreover, we have found that, by heating the peroxide with water at 110°, the same four products are formed but in different proportions. Hence, to account for the formation of cyclopentenealdehyde, it is necessary either to envisage a reaction, inter- or intramolecular in kind, in which the peroxide group acts oxidatively at the double bond and simultaneously disappears entirely from the α-methylene group, or alternatively to look for the source of the cyclopentenealdehyde in the incomplete homogeneity of the hydroperoxide used.

Now it is uncertain whether the changes expressed in Equations (A) and (D), or indeed the peroxide→oxide→ketone-conversion of the above-mentioned trans-annular peroxides, are necessarily always intramolecular ones, but the transformation of pure cyclohexene hydroperoxide into adipic dialdehyde by the action of dilute sulfuric acid must necessarily be intramolecular, since otherwise the formation of α-hydroxyadipic dialdehyde would be inescapable. A conceivable course of reaction is the following, in which coördination of an ethylenic carbon atom with a peroxidic oxygen atom gives an oxonium complex, which on disruption produces momentarily a di-radical, and ultimately (by scission) two aldehyde groups:

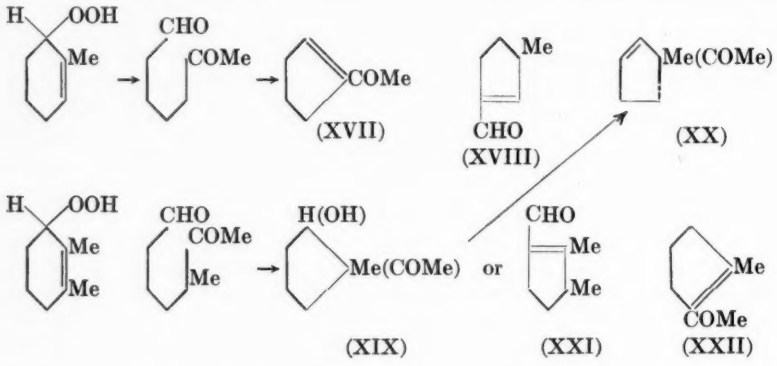


(E)

By this mechanism scission of the cyclohexene could occur without loss of any carbon atoms at a single bond adjacent to the original double bond, and adipic dialdehyde could thus be formed. But if this course of reaction were correct, 1-methylcyclohexene 6-hydroperoxide would be expected to give, with sulfuric acid, 1-acetylcyclopentene (XVII), and the isomeric 3-hydroperoxide similarly to give the aldehyde (XVIII). Likewise 1,2-dimethylcyclohexene 3-hydro-

peroxide should give either 1-acetyl-1-methylcyclopenten-2-ol (XIX) [leading possibly to its dehydration product 1-acetyl-1-methylcyclopentene (XX)] or 2,3-dimethylcyclopenten-1-aldehyde (XXI).

We have found that the normally-formed mixture of 1-methylcyclohexene 6- and 3-hydroperoxides does indeed give 1-acetylcyclopentene (nearly 5% yield), together with 1-methylcyclohexanetriol (40–50% yield) and a little methylcyclohexenol, but no aldehyde or second carbonyl compound is formed; also 1,2-dimethylcyclohexene 3-hydroperoxide gives quite analogously a mixture of a ketone, $C_8H_{12}O$, much 1,2-dimethylcyclohexane-?1,2,3-triol, and a little 1,2-dimethylcyclohexen-3-ol. The ketone $C_8H_{12}O$, however, is found to be, not (XX), but the well-known acetylmethylcyclopentene (XXII), which would result *via* 1,4-diacetylbutane from fission of the cyclohexene ring at the double bond; moreover, the crude ketone contains a little 1,4-diacetylbutane. The formation of only the one observed cyclic carbonyl compound from the isomeric



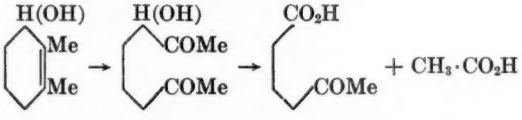
hydroperoxides of 1-methylcyclohexene, and that of the ketone (XXII) from the hydroperoxide of 1,2-dimethylcyclohexene, shows clearly that primary fission of the cyclohexene ring occurs only at the original double bond. It must be concluded, therefore, that the formation of cyclopentenealdehyde, of acetylcyclopentene, and of acetylmethylcyclopentene from the hydroperoxides of cyclohexene, methylcyclohexene, and dimethylcyclohexene, respectively, is due to the presence of some secondary oxidation product in even the best specimens of hydroperoxide obtained.

Special tests with cyclohexene hydroperoxide and methylcyclohexene hydroperoxide showed that the proportion of cyclopentenealdehyde or acetylcyclopentene formed increased very markedly (up to 10% yield) when slightly high-boiling specimens of hydroperoxide of more or less low peroxidic oxygen content were treated with sulfuric acid; but no single specimen of hydroperoxide prepared by our usual procedure (rapid oxidation of the hydrocarbon followed by two distillations with the distillation-bath below 80°), although it showed a correct peroxidic oxygen content, gave a sulfuric acid reaction product which was entirely free from the byproducts in question. The discrepancy concerning the peroxide content is easily explicable, since the best method of determination available is liable to an error of $\pm 5\%$ of the true value; it seems clear, therefore, that some more rigorous procedure than the one adopted would be necessary to prepare the hydroperoxides entirely free from their secondary decomposition products.

The impurity is probably the saturated diol derived from cyclohexene *via* the epoxide (Equation A), and indeed, very small yields of this substance have been isolated on several occasions from the "dimeric" residue left after distillation of the peroxide (see below).

Oxidative action of hydroperoxides in the presence of alkali.—Hock and Gänicke[33] found that when cyclohexene peroxide is shaken with dilute sodium hydroxide solution at a temperature not above 30°, much cyclohexenol is formed, together with a mixture of acids comprising α-hydroxyadipic and adipic acids, as well as small proportions of glutaric acid and volatile fatty acids, which are doubtless formed by further oxidation of hydroxyadipic acid. Cyclohexen-6-ol is the normal hydrolysis product of the hydroperoxide ($R \cdot OOH + H \cdot OH \rightarrow R \cdot OH + H_2O_2$) and we have obtained yields of this alcohol up to 80 per cent of the theoretical. α-Hydroxyadipic acid, formed by the oxidative action of liberated hydrogen peroxide (or possibly to some extent of cyclohexene hydroperoxide) on cyclohexenol or cyclohexene hydroperoxide, is also to be expected, and Hock has shown that this is the principal acidic product (40% of total acids; overall yield, 7.8%). The formation, however, of adipic acid (9% of the total acids in Hock's experiments; overall yield, 1.9%), which we have qualitatively verified, requires explanation, since if the acid is formed from cyclohexene 6-hydroperoxide the α-carbon atom must in this case also have become in some unusual way deoxygenated. We have no doubt that the source of the acid, like that of the cyclopentenealdehyde formed by the action of water, sulfuric acid, heat, or a decomposition catalyst (see below) on the peroxide, is the same nonperoxidic impurity contained in the peroxide used which was referred to above. The 1,2-diol would be likely to undergo ready attack by hydrogen peroxide or alkyl hydroperoxide in alkaline solution.

1,2-Dimethylcyclohexene 3-hydroperoxide gave, with alkali, much 1,2-dimethylcyclohexen-3-ol, together with the expected oxidation products, γ-acetylbutyric and acetic acids. There was formed also in very small yield a high-melting, water-soluble acid (m.p. 196–197°).



1-Methylcyclohexene hydroperoxide gave analogously much methylcyclohexenol and a mixture of several other products, including (1) a little γ-acetylbutyric acid derived from the 3-substituted component of the hydroperoxide mixture, (2) a high-melting, water-soluble *acid*, $C_7H_{10}O_2$ (m.p. 207°), very similar to the one from dimethylcyclohexene hydroperoxide, which remained unreduced on treatment with hydrogen and platinum, but was readily oxidized by permanganate to a highly oxygenated acid (? $C_7H_{10}O_6$) of m.p. 69°, and (3) a syrupy mixture of acids, doubtless containing the oxidative scission products of the 6-hydroperoxide. The high-melting acid, $C_7H_{10}O_2$, was not certainly identified but probably retained the cyclohexane ring intact. Much of the oxidative action promoted by the action of alkali is probably due to the hydrogen peroxide formed by hydrolysis of the hydroperoxides.

Formation of dimeric products.—Stephens[7] reported that, when cyclohexene peroxide was isolated by fractional distillation, there remained behind a considerable liquid residue which, from its empirical composition and molecular

weight, he concluded to be a dimeride of the peroxide containing one peroxide group and probably one active hydrogen atom (found: 0.68 atom) per molecule. We have analyzed a number of these residues from cyclohexene and methylcyclohexene hydroperoxides, and found them to have approximately the characteristics described by Stephens. The amounts of residues formed in our experiments depended largely on the duration of heating during fractionation, or of exposure to ultraviolet light during the oxidation. New quantities of high-boiling residue were certainly formed at each distillation of the peroxide, but a good deal of the residue ordinarily isolated from oxidation products seemed to be formed during the original oxidation. Irradiation of the isolated hydroperoxide in a nitrogen atmosphere gave viscous yellow polymeric residues.

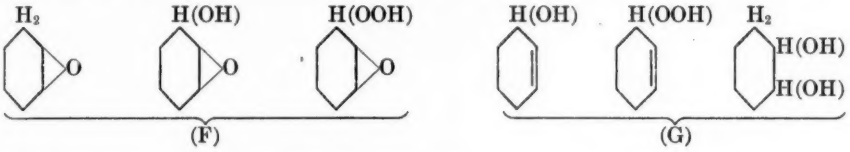
Now, the intermolecular additions which occur during the autoöxidation of these simple unsaturated hydrocarbons are widely encountered in the autoxidation of other olefinic substances, and are specially important in the case of the drying oils (and apparently of rubber), where oxygenated gels and insoluble materials of high molecular weight are ultimately produced. Hence the elucidation of the mechanism of reaction in the simple examples is of considerable interest. This kind of polymerization has been suspected to be a function of peroxidation or of peroxide breakdown, or both, but has not been clearly differentiated from the purely olefinic additions involving carbon-to-carbon intermolecular linking which constitute the ordinary thermal polymerization reactions of unconjugated olefins, although much evidence shows that the thermal polymerizations require for their promotion temperatures well above 200°, whereas the autoöxidation polymerizations can take place at ordinary or only moderately elevated temperatures.

A preliminary examination of many "dimeric" residues from the hydroperoxides of cyclohexene and methylcyclohexene has shown that these materials are highly heterogeneous, although their average composition and molecular weight correspond closely with those required by the strict dimeric formula. This is seen if the residues are extracted with water and with dilute alkali, when usually three types of material, *viz.*, (1) neutral water-insoluble, (2) neutral water-soluble, and (3) acidic water-soluble, are obtainable. None of these fractions is entirely homogeneous, as distillation (with or without preliminary reduction of peroxide groups) shows, and hence the dimeride of even so simple a hydroperoxide as that of cyclohexene must be recognized to contain a considerable range of individuals, formed either by interaction of different products in the autoöxidation mixture or else by oxidative modification (with perhaps some dehydration) of the first-formed dimeric products.

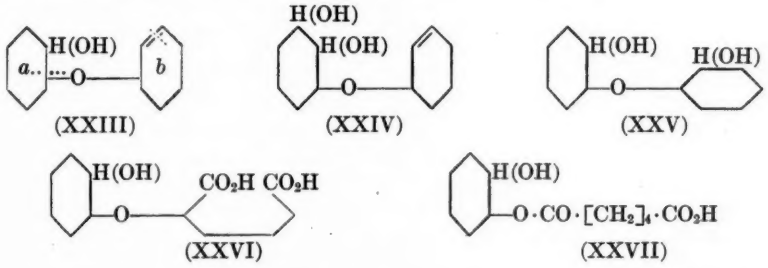
The peroxide content of the residues has been found to depend considerably on the treatment, and especially the thermal treatment, they have received during their formation and isolation. It falls considerably (even as low as about 3%) when the original oxidation process or the subsequent distillation procedure is unduly prolonged or carried out at an unusually high temperature. Indeed, it is clear that heating at 70–100° causes fairly rapid progressive decomposition of the peroxide groups present (including those of unremoved monomeric hydroperoxide), with concomitant oxidative attack at the double bonds, and rapid increase in the complexity ot the system. Isolation of individual dimeric products by fractional distillation is thus well-nigh impossible, and even if all peroxide groups in an original oxidation product are reduced before any distillation is begun, the polymeric residue ultimately obtained is still heterogeneous.

A large proportion of the neutral, water-insoluble fraction obtained from the polymeric residues has a composition, when freed from residual peroxide groups by reduction, between $C_{12}H_{20}O_2$ and $C_{12}H_{18}O$ (as if a mixture of $C_{12}H_{20}O_2$ and its dehydration product), and is almost wholly nonsaponifiable. The main bulk of the neutral, water-soluble material approximates in composition to $C_{12}H_{20}O_3$, and is hydroxylic and hygroscopic. The water-soluble acid fraction is hygroscopic and composed mainly of dimeric molecules of approximate average composition between $C_{12}H_{20}O_5$ and $C_{12}H_{20}O_6$, in which one of the six-carbon rings has apparently undergone oxidative scission, although small quantities of monomeric acidic material (chiefly adipic acid) have been isolated by distillation.

The basis of coupling of molecules appears to us probably to reside largely in the interaction of oxido groups[34] in one reactant molecule (F) with hydroxylic groups in the other (G), and among the possible reactants derived from cyclohexene in the two categories (F) and (G) are:



which may give rise to "dimeric" structures such as (XXIII)–(XXV):



any of which may undergo some degree of dehydration, oxidative scission, *e.g.*, at *a* or *b* in XXIII, or oxidative hydroxylation, *e.g.*, at *b* in XXIII. Whether peroxido links, formed by interaction of oxido groups and hydroperoxido-groups ($RO > R'\cdot O\cdot O\cdot H \rightarrow OH\cdot R\cdot O\cdot O\cdot R'$), are produced at all is uncertain, but hydrogenation experiments indicate clearly that no considerable part of the dimeric product consists of dicyclyl peroxides (reducible to cyclic alcohols). So far as present experiments show, the bulk of the acidic dimeride is unsaponifiable, and is, therefore, to be regarded as composed of further-oxidized dimeride molecules such as (XXVI), rather than of dimeride molecules formed by interaction of an oxido compound and a dibasic acid, *e.g.*, XXVII. The absence of any very large proportion of saponifiable material is probably to be expected in the autoöxidation of a neutral olefin, since the production of free carboxylic acid by oxidative chain scission comes at a late stage in the autoöxidation process, but such absence may well not hold in the case of the autoöxidation of an unsaturated acid, where from the outset of reaction a large concentration of carboxyl groups is available. Indeed, Deatherage and Mattill[35] have already observed that some considerable part of the autoöxida-

tion product of oleic acid is a saponifiable ester, yielding as the alcoholic component, 9,10-dihydroxystearic acid, thus indicating that interaction between oxidostearic acid and the carboxyl group of oleic or oxygenated oleic acid has occurred. The constitution of oleic acid peroxide is described in Part IV.

There is, however, another likely mechanism of autoöxidation polymerization, which may play a more or less important part in the secondary changes (thermally or photochemically promoted) which destroy the hydroperoxide groups first formed. In view of the ready thermal dissociation of dibenzoyl peroxide in liquid media to give free radicals, for which evidence is now strong, it seems probable that free-radical formation ($R \cdot OOH \rightarrow RO— + —OH$) enters into the normal decomposition of hydroperoxides, giving analogous results to those encountered with other decomposing systems[36], and especially giving alcohols and etherlike dimerides ($RO— + RH \rightarrow ROH + R—$ and $R \cdot O \cdot R + H—$). The course of attack on cyclohexene of the free radicals derived from dibenzoyl peroxide will be described later.

SUMMARY

Criegee's conclusion that the peroxide formed by the interaction of molecular oxygen with cyclohexene is a hydroperoxide in which the olefinic unsaturation survives is confirmed. The peroxides formed similarly from 1-methyl- and 1,2-dimethylcyclohexene also are olefin hydroperoxides. The formation of hydroperoxides from olefins and unconjugated polyolefins in general is one of a group of important olefinic reactivities due to the lability of the hydrogen atoms of methylene groups in the α-position to the double bonds.

The hydroperoxide groups decompose spontaneously, and also by the action of heat, giving (1) cyclic epoxides and alcohols, (2) oxidation products, and (3) oxygenated polymeric products. In this decomposition, the hydroperoxide groups act as active oxidizing agents, attacking the carbon chain at the double bond, themselves reverting to hydroxyl groups. Ketones are not formed in recognizable amounts by the spontaneous decomposition of the cyclic hydroperoxides, although they have long been known to appear among the autoöxidation products of monoölefinic terpenes; they are formed, however, to a considerable extent by the violent decomposition promoted by an organic ferrous salt.

The decomposition of olefin hydroperoxides by sulfuric acid, by superheated water, and by alkali has been examined in some detail, the first two reagents causing extensive oxidation of the carbon chain, and the last extensive hydrolysis of the hydroperoxide together with some oxidation. The nature of the products obtained in the sulfuric acid decomposition suggests a reason for the strong promoting influence of organic acids when present during olefin autoöxidations.

The mechanisms of the hydroperoxide decompositions and of the complementary oxidation reactions are considered; also the manner of formation of the polymeric products, which doubtless involves the same fundamental reactivities as are involved in the drying of unsaturated oils.

EXPERIMENTAL

Cyclohexene hydroperoxide.—Carefully purified cyclohexene, b.p. 83°, contained in a quartz flask connected with an oxygen reservoir, was warmed initially to 35°, shaken continuously, and irradiated by means of a mercury

vapor lamp. For this purpose, the flask, containing 100-g. or 200-g. portions of hydrocarbon, was mounted in a mechanical shaker above a small heating bulb, and placed about 6 inches from the lamp. The temperature in the flask usually remained between 35° and 40° without further external heating. The oxygen, from a cylinder, was roughly dried by passing through a calcium chloride tube placed between the reservoir and the reaction flask. No special precautions were taken to absorb small quantities of carbon dioxide produced in the oxidation. Usually, absorption of gas began immediately after the shaking and illumination were started, and proceeded at about 1,500 cc. per hour. The purest peroxide was obtained by rapid absorption of oxygen over a comparatively brief period (3–4 hours), since prolonged exposure to ultraviolet light, with the object of converting a larger portion of the hydrocarbon into peroxide, produced large yields of a high-boiling alteration product, the so-called "dimer" of Stephens. Too slow absorption of oxygen over a long period, arising from feeble illumination, *e.g.*, diffused daylight or light from an ordinary electric bulb, or from a too-low reaction temperature, invariably gave very impure peroxide (containing both low-boiling and high-boiling impurities), owing to the occurrence of secondary peroxidic transformation. In the earlier experiments, the low-boiling impurities escaped notice owing to their high volatility and consequent inclusion with the recovered cyclohexene. For the purpose of studying the secondary products, a few oxidations were conducted more slowly, usually with feebler illumination.

The reaction mixture always contained (1) crude unchanged cyclohexene, (2) a fraction of b.p. about 30°/0.2 mm., (3) the peroxide, and (4) some high-boiling material. These portions were isolated by a preliminary fractionation at 0.5 mm. pressure, and then were examined separately. The peroxide fraction could be stored without any serious deterioration in a refrigerator; specimens of high peroxide content were often found to be little changed after storage for many weeks.

Fraction (2), *b.p.* 30°/0.2 *mm.*—Redistillation through a Dufton column gave a slightly syrupy, oxygenated liquid, b.p. 29–30°/0.2 mm., having P.O.C.[37] 3% (found: C, 72.35; H, 10.3; iodine value, 198.0. Calculated for $C_6H_{10}O$: C, 73.4; H, 10.3%; iodine value, 259.2) and consisting largely of cyclohexen-3-ol (α-naphthylurethane, m.p. 156°; found: C, 76.1; H, 6.25; N, 5.35; calculated for $C_{17}H_{17}O_2N$: C, 76.35; H, 6.4; N, 5.25%) together with a little cyclohexene peroxide. The impure cyclohexanol, after being shaken for a few minutes with 30% aqueous sodium sulfite to reduce cyclohexene peroxide to cyclohexenol, was then peroxide-free, but, although it had the empirical formula $C_6H_{10}O$ (found: C, 73.2; H, 10.2%) it still had only 78.3% of the required unsaturation and less than 80% of the required active hydrogen content (found: iodine value, 207.5; active H, 0.82; calculated for $C_6H_9 \cdot OH$: iodine value, 259.2; active H, 1.03%). The volatile, saturated, oxygenated impurity was the isomeride of cyclohexenol, epoxycyclohexane.

The combined (2) fractions (10.1 g.) from two further portions of cyclohexene which had been oxidized slowly under feebler illumination than usual were refractionated, a Dufton column being used. The major part boiled at 29–30°/0.2 mm. and again consisted of a similar mixture of cyclohexenol, epoxycyclohexane, and a little peroxide (P.O.C. 2.9%; iodine value, 214.2). The epoxycyclohexane, owing to its high reactivity when heated, and especially its ready oxidizability, could best be isolated when the crude oxidation product was immediately reduced with sodium sulfite before fractionation was carried out (see below).

When 2 g. of fraction (2) which had been freed from peroxide by sodium sulfite were heated with 15 cc. of water for 4 hours at 115° in a sealed tube to hydrolyze the epoxide, cyclohexen-3-ol and a crude water-insoluble "dimeric" *oil*, b.p. 112°/0.2 mm. (found: C, 75.6; H, 10.0; iodine value, 180.0. $C_{12}H_{20}O_2$ requires C, 73.4; H, 10.3%) were obtained. When a further 2-g. portion of peroxide-free fraction (2) was hydrolyzed by warming with 20 cc. of *n*-sulfuric acid for 48 hours at 40–45°, cyclohexenol together with a similar "dimeric" oil (found: C, 78.35; H, 10.2%; iodine value, 213.5) were obtained. Several repetitions of these hydrolyses, using (2) fractions isolated from other oxidation products, always failed to give more than very small yields of cyclohexane-1,2-diol, showing that the epoxide was destroyed by either procedure, and apparently underwent reaction with cyclohexanol to give the "dimeric" oil. The formation of epoxycyclohexane was more easily demonstrated by examination of fraction (1).

Fraction (3).—Rapid oxidation of cyclohexene during 4 hours usually gave a product from which were obtained on first fractionation a peroxide fraction of P.O.C. 20–25%, and on second fractionation a 15–20% yield (based on the hydrocarbon taken) of substantially pure cyclohexene 3-hydroperoxide, b.p. 47–48°/0.2 mm. (found: C, 63.25; H, 8.85; P.O.C., 28.0; calculated for $C_6H_{10}O_2$: C, 63.1; H, 8.85%; P.O.C., 28.05%), together with a little less pure (mostly rather low-boiling) peroxide. The unsaturation of the peroxide was conveniently determined by iodine value, but was always a little low (*ca.* $\overline{|0.94}$), owing in part to the occurrence of subsidiary reaction between the peroxide and the potassium iodide reagent. On hydrogenation (Adams's catalyst) the peroxide absorbed 2 mols of hydrogen, giving, in nearly quantitative yield, immediately crystallizable cyclohexanol [3,5-dinitrobenzoate, m.p. 110°, mixed m.p. 110° (found: C, 53.3; H, 4.75; N, 9.60; calculated for $C_{13}H_{14}O_6N_2$: C, 53.05; H, 4.8; N, 9.5%); α-naphthylamine complex with the dinitrobenzoate, m.p. 126°, mixed m.p. 126° (found: C, 62.8; H, 5.1; N, 10.05; calculated for $C_{23}H_{23}O_6N_3$: C, 63.15; H, 5.3; N, 9.6%)]. The rather low-boiling fractions of peroxide showed a low P.O.C., and absorbed only about 1 mol (usually 0.95–0.98 mol) of hydrogen; the hydrogenation product gave, after removal of a small volatile forerun, homogeneous cyclohexanol. This confirmed that the principal normal decomposition product of cyclohexene peroxide is cyclohexenol; and, since in slow oxidations the yield of pure peroxide was diminished and that of the low-boiling fractions increased, the conditions for slow oxidation promoted considerable decomposition.

For the efficient reduction of considerable quantities of the peroxide to cyclohexenol, the former was shaken with well-cooled 30% aqueous sodium sulfite solution, at first cautiously to avoid undue heat development, and later for 2–3 hours on a mechanical shaker. The alcohol, when extracted with ether and rectified, boiled at 65–66°/13 mm.

Fraction (1), *b.p.* 60°/100 *mm.*—To avoid the formation of additional byproducts or the destruction of the original ones through being heated with peroxide during fractional distillation, the reaction product from 100 g. of hydrocarbon (5 hours' oxidation; weight increase, 9.0 g.) was reduced immediately with 30% aqueous sodium sulfite, the reduced product extracted with ether, dried, and freed first from solvent, and then (at slightly reduced pressure) from cyclohexene. The peroxide-free oxidation product gave, on fractionation at reduced pressures under a short column, the fractions: (1) b.p. below 60°/13 mm. (5.0 g.), (2) b.p. 64–65°/12 mm. (13.1 g.), (3) b.p. 80–86°/1 mm. (2.1 g.), (4) b.p. 94–95°/1 mm. (0.3 g.), and a residue (about 1 g.). Of these, (2) was

almost pure cyclohexenol of nearly correct unsaturation and analytical composition (α-naphthylurethane, m.p. 156°; mixed m.p. 156°); (1) was a mixture of this with much epoxycyclohexane, and the higher fractions consisted of heterogeneous "dimeric" materials. The epoxide fraction gave a good yield of transcyclohexane-1,2-diol, m.p. 104°, mixed m.p. 104°, on hydrolysis at 40–45° with *n*-sulfuric acid, and the largest "dimeric" fraction had (assuming homogeneity) an empirical composition approximating to $C_6H_{10}O$ (found: 77.7; H, 10.2; iodine value, 130.8; calculated for $C_6H_{10}O$: C, 73.4; H, 10.3%). Repetition of the experiment with 100 g. of cyclohexene gave precisely comparable results, the yield of epoxide being substantial and the fraction (3) now giving: C, 75.2; H, 10.1%; iodine value, 140.

An attempt to fractionate a further 10 g. of the epoxide fraction at atmospheric pressure caused considerable interaction of the component materials as well as dehydration, with formation of (1) a small quantity of highly unsaturated hydrocarbon, apparently cyclohexadiene, (2) cyclohexane-1,2-diol, m.p. 104° (found: C, 62.0; H, 10.4; calculated for $C_6H_{12}O_2$: C, 62.0; H, 10.4%), and a viscous residual liquid. A tolerably pure epoxide fraction, of b.p. 110–120°, convertible into cyclohexanediol, was, however, obtained.

Action of heat on the hydroperoxide.—When cyclohexene hydroperoxide was heated, its peroxidic character diminished. The change was relatively slow at room temperature in diffused daylight, but much more rapid when the peroxide was distilled from a bath at 70–80°. A peroxide fraction (16.5 g.) which, when separated from the crude oxidation product by one distillation at 0.5 mm. pressure, had P.O.C. 24.2%, gave on redistillation at the same pressure the fractions (1) b.p. 30–35°, P.O.C. 2–3% (1.8 g.); (2) b.p. 44–45°, P.O.C. 20.1% (10 g.); (3) b.p. 45–46°, P.O.C. 28.5% (3.6 g.); and a high-boiling residue (0.8 g.). The chief low-boiling product was cyclohexen-3-ol, but no epoxycyclohexane was identified. The high-boiling residue approximated in composition to the formula $C_6H_{10}O_2$ (found: C, 63.75; H, 9.05; calculated for $C_6H_{10}O_2$: C, 63.1; H, 8.85%) and had P.O.C. 14.3%: it thus corresponded with Stephens's "dimeride".

Action of ultraviolet light on the hydroperoxide.—Peroxide of P.O.C. 27.8% (4 g.) was placed in a quartz flask and the air carefully displaced by oxygen-free nitrogen. The flask was shaken and simultaneously illuminated by ultraviolet light at about 35° for 6 hours. The viscosity of the peroxide increased, its color changed to light yellow, and its P.O.C. fell by about one-half to 14.5%; its empirical composition, however, was little or not at all changed (found: C, 63.8; H, 9.0%). A portion (2.8 g.) of the irradiated material was immediately hydrogenated in alcohol (Adams's catalyst). It absorbed 559 cc. at N.T.P., *i.e.*, one-half of that required (1090.4 cc.) for reducing one double bond and the ·OOH group in $C_6H_9 \cdot OOH$. In view of the observed overall fall of one-half of the total P.O.C., due to irradiation, the overall olefinic unsaturation must likewise have diminished by one-half (282 cc. of hydrogen at N.T.P. used for reducing peroxide, 277 cc. for reducing double bond). Thus an overall loss by decomposition of one hydroperoxide group was accompanied by the saturation of one double bond. The product, when freed from alcohol, had P.O.C. $< 0.02\%$; it gave on distillation (1) 1.1 g. of cyclohexanol, b.p. 63–64°/14 mm., (2) 0.6 g. of "dimeric" material, b.p. 110–176°/0.5 mm., and (3) 0.4 g. of undistilled residue.

3.2 grams of peroxide of P.O.C. 27.8% (found: C, 63.2; H, 9.0%) were irradiated for 6 hours at approximately 35° as above, but in an atmosphere of oxygen. Some oxygen was absorbed (150 cc.) and the pale yellow liquid

product then had P.O.C. 14.35% [found: C, 58.75; H, 8.2; O (by difference), 33.05%]. On hydrogenation the product (2.6 g.) absorbed 403 cc. (average of 0.64 mol) of hydrogen at N.T.P., so during the irradiation both absorption of oxygen and some saturation of the double bond had occurred. The product consisted of a little cyclohexenol (0.6 g.) and "dimeric" material of b.p. 120°/0.5 mm. and above.

Action of the hydroperoxide on cyclohexene.—When equimolecular weights of the peroxide (3.9 g.) and pure hydrocarbon (2.8 g.) were exposed in a flask to diffused daylight for 4 weeks at room temperature, and the product subsequently hydrogenated, it was found to have undergone no serious reduction of unsaturation (H_2 absorbed, 2250 cc. at N.T.P.; theory, 2295 cc.). When a similar mixture (3 g. of each component) was heated for 5 hours on a water-bath, the product was found on fractionation to consist of crude cyclohexene (2.4 g.), cyclohexenol (0.8 g.), unchanged peroxide (1.4 g.), "dimer" (0.4 g.), and undistilled residue (0.5 g.). After the lowest-boiling fractions had been heated with water at 115° in a sealed tube to hydrolyze any epoxycyclohexane present, only a small yield of cyclohexane-1,2-diol, m.p. 104°, could be isolated from the product.

Action of the hydroperoxide on cyclohexen-3-ol.—The alcohol (3.4 g.) and pure peroxide (3.5 g.) were heated together at 100° for 5 hours. The pale yellow liquid product was reduced with sodium sulfite solution and fractionated. The product consisted almost entirely of cyclohexenol, but there were a small fraction (0.3 g.) of b.p. 100–105°/13 mm. and a higher-boiling residue (0.3 g.). The volatile fraction gave on heating with water in a sealed tube at 110° a small yield of cyclohexane-1,2,3-triol (see below). No oxidation of cyclohexenol to cyclohexenone had occurred.

A similar mixture of alcohol and hydrocarbon in a quartz flask was shaken and simultaneously exposed to ultraviolet light at 35° in a nitrogen atmosphere. The product, after being freed from peroxide by shaking it with sodium sulfite, was fractionated: it consisted of cyclohexenol (76%) and "dimeric" material, of b.p. 110°/13 mm. and above. No ketone was detected.

Action of dilute sulfuric acid on the hydroperoxide.—Crude, undistilled cyclohexene hydroperoxide, derived by slow oxidation of cyclohexene under feeble ultraviolet illumination (24 hours at 30–40°) and freed from unchanged cyclohexene by distillation at 12 mm. pressure (4 g.), was mixed with *n*-sulfuric acid (20 cc.) and kept at 40–45° for 1 week. The undissolved oil was collected with a little ether, and the clear aqueous layer then neutralized and evaporated to dryness. The residue yielded (1) by extraction with ethyl acetate crude cyclohexanetriol, b.p. 115–120°/1 mm. (1 g.), which on crystallization from ethyl acetate melted at 108–111° and on recrystallization at 124° (found: C, 54.65; H, 9.2; calculated for $C_6H_{12}O_3$: C, 54.5; H, 9.15%), and (2) by acidification, followed by extraction with ether, a syrupy acidic oxidation product of high b.p. The water-insoluble oil when worked up gave cyclopentene-1-aldehyde, b.p. 55–60°/13 mm. (0.6 g.) [dimedone, m.p. 123–124°; semicarbazone, m.p. 209° (found: C, 54.5; H, 7.25; N, 26.7; calculated for $C_7H_{11}ON_3$: C, 54.85; H, 7.25; N, 27.45%)], cyclohexenol contaminated with a little unchanged peroxide, b.p. 65–70° (0.5 g.), and higher-boiling hydroxylic "dimeric" substances (1.6 g.). Repetitions of the experiment with hydroperoxide of correct or slightly low P.O.C. gave also cyclohexanetriol (35–45% yield), cyclohexenol (10–15%), water-insoluble hydroxylic oils, for the most part distillable (b.p. 70–100°/13 mm.) (about 10–15%), syrupy acidic material (about 10% yield), and always some cyclopentenealdehyde. The yield of aldehyde in-

creased considerably with decreasing P.O.C. of the hydroperoxide specimen but was never less than 2–3%, even when derived from specimens of correct P.O.C.

Action of water on the hydroperoxide.—When the hydroperoxide (5.3 g.) of P.O.C. 17% was heated for 3 hours with water in a sealed tube at 115°, a brown oily layer (3.2 g.) and an aqueous layer resulted. The former when distilled gave cyclopentene-1-aldehyde (0.8 g.) and about equal quantities of unchanged hydroperoxide, cyclohexenol, and "dimeric" oil; the latter, on extraction with ethyl acetate, gave cyclohexanetriol (1 g.) and a distillable hygroscopic syrupy acid (0.5 g.). The last of these was a nonhomogeneous oxidation product, b.p. about *ca.* 100°/2 mm. (found: C, 58.65; H, 8.55%).

Action of caustic alkali on the hydroperoxide.—The peroxide (9.3 g.) of P.O.C. 27.0%, when mechanically shaken with *n*-sodium hydroxide (150 cc.) for 2 hours, dissolved to give a yellow solution. The product after having stood for 24 hours at room temperature gave on extraction with ether cyclohexen-3-ol (6.6 g.; 82% yield). The alkaline liquor on acidification and extraction with ether gave a very small yield of adipic acid, m.p. 152° (mixed m.p. 152°), and some syrupy acid; a further amount of syrupy acid was obtained by continuous extraction with ether. The nature of this heterogeneous syrupy acid has been investigated by Hock and Gänicke[33].

1-Methylcyclohexene Hydroperoxide and its Transformation Products

1-Methylcyclohexene hydroperoxide, 1-methylcyclohexene 1,2-epoxide and 1-methylcyclohexenol.—Methylcyclohexene, b.p. 110–111° (90 g.), obtained by dehydration of 1-methylcyclohexanol in presence of a little iodine, was oxidized in a quartz flask at about 35°, as described for cyclohexene (above). Absorption of gas occurred rapidly (1.5–2.5 l. per hour; 9,800 cc. in 5.5 hours), and the product gave on distillation at 15 mm. pressure unchanged methylcyclohexene (50 g.; nearly 60% recovery) and colorless, crude peroxide (39.1 g.). The latter gave on fractionation at 0.2 mm.: (1) b.p. 40–41°, P.O.C. 4.9% (11.8 g.), (2) b.p. 52–58°, P.O.C. 20.95% (6.6 g.), (3) b.p. 60–67°, P.O.C. 26% (5.0 g.), (4) b.p. 67–70°, P.O.C. 24.0% (15.7 g.), and a "dimeric" residue, P.O.C. about 25% (15.0 g.).

The fraction (1), when freed from peroxide with sodium sulfite solution, was a volatile nonketonic liquid (unreactive with the Girard reagent "T"), b.p. 65–67°/13 mm., having nearly the empirical composition of methylcyclohexenol but less than one-half its unsaturation (found: C, 74.05; H, 10.95; iodine value, 103.9, 104.3; calculated for $C_7H_{12}O$: C, 74.95; H, 10.7; iodine value, 226.9). This was a mixture of methylcyclohexenol (about 50%) with 1-methylcyclohexene 1,2-epoxide, and gave on hydrolysis with *N* sulfuric acid (2.2 g. warmed with 15 cc. of acid for 1 week at 40–45°) a 30% yield of trans-1-methylcyclohexane-1,2-diol (prisms, m.p. 84°, from light petroleum-chloroform; lit., m.p. 83.5°) (found: C, 64.6; H, 11.0; calculated for $C_7H_{14}O$: C, 64.6; H, 10.85%), together with a little methylcyclohexenol, b.p. 66–67°/13 mm. (0.3 g.) (see below) and a "dimeric" fraction, b.p. 130–132°/13 mm. (0.5 g.). Hydrolysis of a similar epoxide-alcohol fraction with water at 115° gave a similar result, but a smaller yield of diol.

The fraction (3) consisted of nearly pure 1-methylcyclohexene-6 (with some 3)-hydroperoxide (P.O.C. 26. $C_7H_{12}O_2$ requires P.O.C., 25%), and fraction (4) was only a little inferior in P.O.C. to (3). Redistillation caused some

secondary change, involving decomposition of the peroxide groups in a part of the material. The fraction of b.p. 64–67°/0.2 mm. so obtained had P.O.C. 99% of theory, but was not quite pure (found: C, 66.1; H, 9.75; active H, 0.85. $C_7H_{12}O_2$ requires C, 65.6; H, 9.4; active H, 0.78%).

When the hydroperoxide (3.6 g.) was shaken with 30% aqueous sodium sulfite (200 cc.) for 3 hours and then similarly treated with fresh sulfite, reduction (less facile than with cyclohexene hydroperoxide) occurred. The product, when extracted with ether, and dried, gave on distillation 1-methylcyclohexen-6 (with some 3)-ol containing a little of a saturated secondary product (found: C, 74.0; H, 10.1; iodine value, 206.3, 208.0. $C_7H_{12}O$ requires C, 74.95; H, 10.7%; iodine value, 226.7). The impure alcohol gave an oily 3,5-dinitrobenzoate, from which a crystalline α-naphthylamine *complex*, m.p. 95–96° (found: N, 9.35. $C_{24}H_{23}O_6N_3$ requires N, 9.35%), was obtained.

Hydrogenation of the hydroperoxide (11.6 g.; P.O.C. 22%) in alcohol by means of Adams's catalyst took place more slowly than with cyclohexene hydroperoxide. After 18 hours, 3720 cc. of hydrogen at N.T.P. had been absorbed (calculated for $|\overline{\overline{0.88}}$ and 0.88 ·OOH group in peroxide of P.O.C. 22%: 3572 cc.). The centrifuged product gave on distillation crude 1-methylcyclohexanol, b.p. 60–76°/13 mm. (found: C, 71.85; H, 11.65; calculated for $C_7H_{14}O$: C, 73.35; H, 12.3%), the *α-naphthylurethane*, from which contained two difficultly-separable isomerides. Two crystallizations of the urethane from petroleum (b.p. 60–80°) have a product, m.p. 123° (found: C, 76.6; H, 7.65; N, 5.3. $C_{18}H_{21}O_2N$ requires C, 76.3; H, 7.4; N, 5.0%), which depressed the m.p. of the urethane of authentic 1-methylcyclohexane-3-ol (m.p. 123°; mixed m.p. 102°), but apparently consisted mainly of the urethane of 1-methylcyclohexan-2-ol (m.p. 154°; mixed m.p. 139°). Oxidation of the crude alcohol in aqueous acetic acid with chromic acid gave a ketone, b.p. 80–86°/60 mm., the semicarbazone from which melted at 175°, and after two crystallizations from methyl alcohol at 191° (found: C, 56.6; H, 9.1; calculated for $C_8H_{15}ON_3$: C, 56.8; H, 8.94%). This was identical with the semicarbazone of authentic 1-methylcyclohexan-2-one, m.p. 192° (mixed m.p. 191–192°). The mother liquors of both urethane and semicarbazone each contained a second derivative in minor amount, difficultly purifiable but, in view of later observations (below), without doubt derived from 1-methylcyclohexan-3-ol and -3-one, respectively. It follows, therefore, that the hydroperoxide and methylcyclohexenol derived from 1-methylcyclohexene contained both the 6-substituted (major) and the 3-substituted (minor) isomerides.

Action of dilute sulfuric acid on the hydroperoxide.—The hydroperoxide (4 g.) was warmed to 45° for 100–120 hours with *N* sulfuric acid (20 cc.). The product contained an oily and an aqueous layer. The latter gave on neutralization with alkali, evaporation, and extraction with ether, 1-*methylcyclohexane*-1,2,3-*triol*, b.p. 152–154°/1 mm., crystallizing from ethyl acetate in small prisms, m.p. 95° (1.9 g.) (found: C, 57.1; H, 9.55. $C_7H_{14}O_3$ requires C, 57.5; H, 9.6%), and the former on distillation at 13 mm. pressure gave three fractions, of b.p. 58°, 80–90°, and 114–120°, severally. The first of these fractions was a slightly impure ketone, $C_7H_{10}O$ (found: C, 75.35; H, 9.3; calculated: C, 76.3; H, 9.15%), recognized by its semicarbazone, m.p. 205° (found: C, 57.3; H, 7.75; N, 24.9; calculated for $C_8H_{13}ON_3$: C, 57.45; H, 7.8; N, 25.15%), and oxime, m.p. 91° (found: C, 67.1; H, 8.7; N, 11.3; calculated for $C_7H_{11}ON$: C, 67.15; H, 8.85; N, 11.2%), to be 1-acetylcyclopentene (Wallach[38] reports semicarbazone, m.p. 203–204°, and oxime, m.p. 91°). The higher-boiling fractions consisted of a little crude methylcyclohexenol containing unchanged peroxide and

"dimeric" products. The neutral sodium salts gave, on acidification and extraction with ether, a syrupy, acidic product.

Action of caustic alkali on the hydroperoxide.—When the hydroperoxide (6.4 g.) was shaken for 3 hours with *N* sodium hydroxide (150 cc.), kept overnight, and then warmed at 30° for 3 hours, an oil which proved to be a mixture of 6- and 3-hydroxy-1-methylcyclohexene separated, and was collected in a little ether. The crude alcohol was retreated with alkali to remove the last traces of peroxide, and then distilled. It boiled at 66–68°/13 mm. (found: C, 74.5; H, 10.55; calculated for $C_7H_{12}O$: C, 74.95; H, 10.7%); yield 89%. The alkaline solution gave, on neutralization, evaporation and final extraction with ether of the acidified residue, a brown syrupy acid (1.0 g.), from which some large prisms of a monobasic *acid*, $C_7H_{10}O_2$, m.p. 207°, separated (found: C, 66.6; H, 8.0; equiv., 125.7. $C_7H_{10}O_2$ requires C, 66.65; H, 8.0%; equiv., 126.0). The solid acid remained unattacked when shaken in alcohol with hydrogen and Adams's catalyst; it was, however, readily attacked by permanganate, giving thereby an acid of high oxygen content (? $C_7H_{12}O_6$), crystallizing in minute stout plates, m.p. 69°, but obtained in too small amount to be adequately examined. The residual syrupy acid was heterogeneous, a minor part consisting of γ-acetylbutyric acid, isolated in the form of its hydrated semicarbazone, $C_7H_{13}O_3N_3,H_2O$, of m.p. 170° (decomp.) (slow heating), which became anhydrous at 100°[39] (found: C, 45.15; H, 6.9; calculated for $C_7H_{13}O_3N_3$: C, 44.9; H, 7.0%), and the major part persisting as an intractably syrupy acid which was not further examined.

1,2-Dimethylcyclohexene-3-Hydroperoxide and its Transformation Products

1,2-Dimethylcyclohexene-3-hydroperoxide, 1,2-dimethylcyclohexene 1,2-epoxide, and 1,2-dimethylcyclohexen-3-ol.—Dimethylcyclohexene, b.p. 136–137° (71 g.), obtained by dehydration in presence of iodine of 1.2-dimethylcyclohexan-1-ol, formed from 2-methylcyclohexanone and methylmagnesium iodide, was oxidized at 23° in a quartz flask. In 95 minutes, 5.8 l. (7.5 g.) of oxygen were absorbed. Distillation of unchanged hydrocarbon (41.5 g.) gave a residue of crude oxygenated products (35.6 g.), which on fractionation at 0.5 mm. pressure gave the fractions: (1) b.p. 40–50° (5.1 g.; P.O.C., 4.8%), (2) b.p. 55–64° (8.8 g.; P.O.C., 19.4%); (3) b.p. 64–69° (6.4 g.; P.O.C., 23.5%); (4) b.p. 70–73° (6.1 g.; P.O.C., 22.3%), and a heterogeneous "dimeric" residue (6.0 g.; P.O.C., 9.8%). Of these fractions, (3) and (4) consisted of practically pure *1,2-dimethylcyclohexane 3-hydroperoxide*, b.p. 67–70°/0.5 mm. (found: C, 67.7; H, 9.9. $C_8H_{14}O_2$ requires C, 67.55; H, 9.9; P.O.C., 22.2%), and fraction (2) also consisted mainly of hydroperoxide. Fraction (1), when it had been entirely freed from traces of unchanged hydroperoxide by treatment with sodium sulfite, and refractionated, gave a low-boiling portion containing 30–40% of a saturated component, and a higher-boiling portion (2.5 g.) of nearly pure dimethylcyclohexen-3-ol (iodine value, 191.5. Theory, 201.5), oxidizable to dimethylcyclohexen-3-one (see below). The lower-boiling portion was crude 1,2-dimethylcyclohexene-1,2-epoxide and gave, on hydrolysis with *N* sulfuric acid, *trans*-1,2-dimethylcyclohexane-1,2-diol, m.p. 92° (0.5 g.) (found: C, 66.4; H, 11.25; calculated for $C_8H_{16}O_2$: C, 66.6; H, 11.2%). Refractionation at atmospheric pressure of the unchanged hydrocarbon, after it had been well dried with anhydrous magnesium sulfate (calcium chloride proved unsatisfactory), gave 4 g. of crude epoxide, from which by hydrolysis with sulfuric acid, the *trans*-diol, m.p. 92° (1.5 g.) was obtained.

Action of dilute sulfuric acid on the hydroperoxide.—The hydroperoxide (4.6 g.), when treated with *N* sulfuric acid as above, gave a water-soluble fraction (2.0 g.) and a water-insoluble fraction (2.6 g.). The former gave, on distillation at 0.5 mm. pressure, 1,2-*dimethylcyclohexane*-1,2,3-*triol*, which crystallized from ethyl acetate-ether in colorless prisms, m.p. 109° (found: C, 59.8; H, 10.1. $C_8H_{16}O_3$ requires C, 60.0; H, 10.1%); the latter gave on distillation (1) a ketonic fraction (free from aldehyde) of b.p. 74–80°/13 mm. (0.93 g.), (2) an alcohol, identified as somewhat impure 1,2-dimethylcyclohexen-3-ol (see above), and (3) a small "dimeric" residue. The ketone yielded a semicarbazone and an oxime which, when recrystallized from alcohol, melted, respectively, at 219° and 85°. These compounds proved on direct comparison to be identical with the corresponding derivatives (m.p.'s 221° and 86°, respectively) of 1-acetyl-2-methylcyclopentene, the requisite ketone (b.p. 72–74°/13 mm.) being synthesized from 1,2-dimethylcyclohexene by successively ozonizing it, heating the ozonide with water, and finally heating the resulting 1,4-diacetylbutane (b.p. 110°/13 mm.) with either *N* sulfuric acid or alcoholic potassium hydroxide.

Action of caustic alkali on the hydroperoxide.—The hydroperoxide was shaken with *N* sodium hydroxide solution for 3–4 hours, the mixture allowed to stand overnight, and then warmed to 30–40° for 2 hours. The product when worked up gave an alcohol (80% yield) and a syrupy acid (15–20% yield). The alcohol, after being freed from a little unchanged peroxide by renewed shaking with alkali, proved to be 1,2-*dimethylcyclohexen*-3-*ol*, b.p. 80–82°/13 mm. (found: C, 75.35; H, 11.5; iodine value, 202. $C_8H_{14}O$ requires C, 76.1; H, 11.2%; iodine value, 201.5). This gave an *α-naphthylurethane*, m.p. 139–140° (found: C, 77.0; H, 7.3. $C_{19}H_{21}O_2N$ requires C, 77.25; H, 7.15%), was oxidizable by chromic acid to 1,2-dimethylcyclohexene-3-one [semicarbazone, m.p. 224–225°[40]; found: C, 59.4; H, 8.4; calculated for $C_9H_{15}ON_3$: C, 59.6; H, 8.35%], and absorbed 1 mol of hydrogen per mol in presence of palladium-charcoal. The syrupy acid deposited (on one occasion only) a few colorless prismatic crystals, insufficient for adequate purification, of an acid, m.p. 196–197° (found: C, 65.45; H, 7.95%), which was similar to, or possibly identical with, the acid of m.p. 207° derived similarly from 1-methylcyclohexene hydroperoxide; the main bulk, however, always consisted of γ-acetylbutyric acid [semicarbazone, m.p. 170°, identical with that obtained above in a corresponding way from 1-methylcyclohexene hydroperoxide (found: C, 44.65; H, 6.9%)].

Rapid Decomposition of Peroxides

Cyclohexene hydroperoxide.—When a few mg. of ferrous phthalocyanine was dropped into portions of 4 g. of fairly pure peroxide, there was usually a flash of light, and always the liquid became warm and soon boiled. A little water separated, the liquid darkened in color, and aldehydic vapor, but no oxygen was evolved. Direct distillation of the liquid products when reaction subsided caused renewed reaction, with formation of much high-boiling material: it was better to extract the main products with light petroleum, leaving behind the catalyst and a little ether-soluble oxidation product. Distillation at reduced pressure then gave, first, a fraction of strong aldehydic odor and reaction, and later, fractions which contained much cyclohexenol and unchanged peroxide. The aldehydic fraction, b.p. 60–62°/14 mm., was heterogeneous, giving a crude semicarbazone, m.p. 155–165°, containing two isomerides $C_7H_{11}ON_3$ (found: C, 54.95; H, 7.25; calculated: C, 54.85; H, 7.25%). By repeated recrystalliza-

tion from alcohol, the higher-melting component, m.p. 205°, was isolated in small yield and identified as cyclopentene-1-aldehyde semicarbazone; the major component, however, could not be fully freed from its isomeride (m.p. 157–163°), and appeared to consist mainly of cyclohexen-3-one semicarbazone, m.p. 161°.

When the hydroperoxide was gradually heated in an open test-tube, standing in an oil-bath, very vigorous decomposition set in at about 120°, steam and volatile vapors being evolved, the latter containing cyclopentene-1-aldehyde.

1-*Methylcyclohexene hydroperoxide.*—Treatment of this peroxide with ferrous phthalocyanine as above caused development of heat, darkening in color, and vigorous ebullition. The products, if freed from catalyst before being distilled, were almost completely distillable. The b.p. of the distillate rose progressively from 80°/13 mm. to 122°/11 mm. No exhaustive examination of the fractions was made, but much of the material consisted of methylcyclohexenol and unchanged hydroperoxide; the fractions boiling between 64° and 78° at 1 mm., however, contained a moderate proportion of ketone, which gave mixtures of two semicarbazones, (1) m.p. 207–208° (slow heating), identified as 1-methylcyclohexen-6-one semicarbazone (m.p. 207–208°[41]; found: C, 57.5; H, 7.95; calculated for $C_8H_{13}ON_3$: C, 57.45; H, 7.85%) by comparison with the semicarbazone of the ketone formed by oxidation of 1-methylcyclohexen-6-ol with chromic acid (mixed m.p. 207–208°), and (2) m.p. 198–200°, rather more readily soluble in alcohol than (1). This last compound appeared to be isomeric with both (1) and 1-acetylcyclopentenesemicarbazone (m.p. 207–208°; mixed m.p. 190–192°), and hence was probably 1-methylcyclohexen-3-one-semicarbazone (m.p. 198°, 199–200°; Fargher and Perkin[42]; found: C, 57.35; H, 8.0%).

1,2-*Dimethylcyclopentene hydroperoxide.*—This peroxide, when similarly decomposed with ferrous phthalocyanine, gave a comparable heterogeneous product, the most volatile portion of which, b.p. 56–63°/1 mm., contained a ketonic component. This formed a semicarbazone, m.p. 219°, raised by recrystallization from alcohol to 224–225°. This semicarbazone closely resembled in physical properties authentic 1,2-dimethylcyclohexen-3-one semicarbazone, m.p. 224–225°, derived by oxidation of 1,2-dimethylcyclohexen-3-ol with chromic acid; also it caused no depression of m.p. when heated with the latter. On the other hand, it depressed the m.p. of authentic 1-acetyl-2-methylcyclopentenesemicarbazone, m.p. 221° (mixed m.p. 209°).

Dimeric Products

From cyclohexene hydroperoxide.—From all autoöxidation products there remained, after distillation of the hydroperoxides at 0.2–1.0 mm. pressure, a rather viscous, yellow, peroxidic oil which was partly distillable below 1 mm. pressure. The proportion of this polymeric residue varied considerably (from 25 to 40% of the total oxygenated material) with change in the conditions of oxidation, and increased markedly with prolongation of heating during the oxidation or distillation, and apparently also with prolongation of exposure to ultraviolet light. When the crude oxidation product was freed from active peroxide groups by reduction with sodium sulfite, the absorption of oxygen ended immediately, and the yield of dimeric material on subsequent distillation fell to 15–20%. Each time the pure hydroperoxide was distilled, a fresh small quantity of high-boiling residue was left; furthermore, when the carefully

fractionated hydroperoxide was irradiated for several hours in an atmosphere of pure nitrogen, a considerable high-boiling, yellow residue remained on distillation.

When oxidation was conducted rapidly at 30–35° and the monomeric products were removed as efficiently and rapidly as possible at pressures below 1 mm., the residue (undistilled) approximated in average composition to that required for the empirical formula $C_6H_{10}O_2$, as shown by analytical data from residues from three sources: (1) from normal oxidation (found: 63.85; H, 8.95; P.O.C., 14.7%; iodine value, 122.0; calculated for $C_{12}H_{20}O_4$: C, 63.2; H, 8.8; iodine value, for $|\overline{=}_2$, 222.8; P.O.C. for 2 ·OOH groups, 28.6%); (2) from irradiation of hydroperoxide in nitrogen (found: C, 63.8; H, 9.0; P.O.C., 14.5%); (3) from redistillation of rectified hydroperoxide (found: C, 63.75; H, 9.85; P.O.C., 12.65%). When the oxidation was conducted at higher temperatures, *e.g.*, 50–60°, or the process was unduly prolonged owing to feeble irradiation, or temperatures well above 70° were used in distilling off the monomeric hydroperoxide, then the P.O.C. of the residue was low, ranging down to 3%. Direct heating of the residue for a short time at 100° caused a marked decrease in P.O.C. Since there was great difficulty in completely distilling the monomeric peroxide from the residue, while avoiding excessive heating, the figures for the P.O.C. of the polymeric substance (distillation bath below 80°) were probably somewhat high.

Fractional distillation at 0.5 mm. pressure of a normal oxidation residue having P.O.C. 12.6% gave fractions of both varied boiling point (from 40° to 98°) and P.O.C., leaving a brown, almost peroxide-free mass in the still. Fractional distillation of a similar residue which had first been reduced to nearly zero P.O.C. with sodium sulfite gave, on distillation, fractions ranging in b.p. from 50° to 130° at 0.5 mm., and there remained a viscous yellow residue. A similar oxidation residue of average empirical composition corresponding nearly to $C_6H_{10}O_2$, and having P.O.C. 14.7%, and iodine value of 122, absorbed approximately 2 mols of hydrogen in presence of Adams's catalyst, and then gave on distillation at 0.5 mm. pressure a little cyclohexanol (10% yield), a little cyclohexane-1,2-diol (1% yield), distillable "dimeric" substances ranging in b.p. from 60° to 120°, and an undistillable viscous residue. When reunited and extracted with hot water, these high-boiling substances gave an extract (about $\frac{1}{6}$ of the total), which on redistillation at 0.5 mm. pressure gave almost equal fractions of b.p. (1) 84° and (2) 96° severally. These fractions had each approximately the empirical composition $C_6H_{10}O$ [found: (1) C, 73.65; H, 10.2; (2) C, 72.15; H, 10.1; calculated for $C_6H_{10}O$: C, 73.4; H, 10.3%].

A normal oxidation residue (9.8 g.), when immediately extracted with hot water, gave an aqueous extract containing a pale yellow, acid syrup (3.5 g.), and an undissolved neutral yellow oil (A). This syrup was divided by the action of dilute alkali into a neutral (B) and an acidic portion (C). All these fractions were in the main distillable, but none boiled constantly. The neutral fraction (A) boiled principally between 80° and 90° at 1 mm., and varied somewhat in compoitsion from fraction to fraction and from preparation to preparation [*e.g.*, found for the main fractions of different peroxide-free preparations, (1) b.p. approx. 84°/1 mm., and (2) b.p. 80–86°/1 mm.: C, (1) 73.65, (2) 76.52; H, (1) 10.2, (2) 9.77. $C_{12}H_{20}O_2$ requires C, 73.4; H, 10.3%. $C_{12}H_{18}O$ requires C, 80.85; H, 10.2%]. The neutral, water-soluble fraction (B) had *M*, 320 (in benzene) and distilled for the most part at approximately 115°/13 mm. It was hygroscopic, reacted readily with benzoyl chloride, and was probably dihydroxylic (found: C, 66.1; H, 9.9. $C_{12}H_{20}O_3$ requires C, 67.9; H, 8.5%).

The hygroscopic, acidic, water-soluble fraction (C) had M, 231 (in benzene) and gave a main fraction of b.p. approximately 135°/13 mm. (found: C, 56.7; H, 8.5%).

From 1-methylcyclohexene hydroperoxide.—The residue left when the hydroperoxide of 1-methylcyclohexene was distilled from the crude oxidation product (found: C, 64.1; H, 9.0; calculated for $C_7H_{12}O_2$: C, 65.6; H, 9.4%) gave, on extraction with water, a neutral, water-insoluble oil and an acidic, water-soluble syrup. Both these substances were almost wholly distillable but heterogeneous, boiling over the ranges 110–128°/1 mm. and 74–108°/1 mm., respectively. They were not examined further.

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[10] This expectation is most completely fulfilled in the analogous attack on the α-methylene groups of olefins by selenium dioxide in the presence of acetic acid. Here, acetoxy groups become substituted in the following systems at the points marked by asterisks (Guillemonat, *Ann. chim.* **11**, 143 (1939):

$$H_3C\overset{*}{C}(CH_3) : CHCH_3,\ H_3C\overset{*}{C}H_2C(CH_3) : CH_2,$$

$$H_3\overset{*}{C}C(C_3H_7)^{\beta}: CHCH_3,\ H_3\overset{*}{C}C(CH_3) : CHC_2H_5,\ H_3C\overset{*}{C}H_2C(C_6H_5) : CHCH_3,$$

$$H_3C\overset{*}{C}H_2CH : CHCH_3,\ H_2\overset{*}{C}RC(C_2H_5) : CHCH_2R,\ \text{and}\ HC(CH_3)RCH : C\overset{*}{H}CH_2R.$$

The similarity of selenium dioxide oxidation to peroxidation is remarkable.
[11] It is difficult, in experiments of this kind, to demonstrate with certainty that the cyclohexene oxide and cyclohexanol are formed in molecularly equivalent amounts.
[12] Some proportion of organic acid formed by chain scission is likely to appear as reaction proceeds, or more rapidly at the temperature of distillation.
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[22] Cook called the ketone 1-methylcyclohexen-3-one and the cyclic alcohol 1-methylcyclohexen-3-ol, whereas Dupont considered his ketone and alcohol to be 1-methylcyclohexen-6-one and 1-methylcyclohexen-6-ol, respectively. As indicated above, owing to the formation in the original oxidation of two isomeric forms of the hydroperoxide, both the 6-alcohol and the 3-alcohol could hardly fail to be present in Cook's and Dupont's preparations; and if the ketone is formed directly from the alcohol or from the parent peroxide, then both the 6-ketone and the 3-ketone would also be present.
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[27] Morrell *et al.*, *J. Soc. Chem. Ind.* **50**, 27T (1931); **55**, 237T (1936); **58**, 159T (1939); *J. Oil Colour Chem.* **23**, 103 (1940).
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[29] Bloomfield, *J. Soc. Chem. Ind.* **54**, 2T (1935).
[30] Bolland, *Trans. Inst. Rubber Ind.* **16**, 267 (1941).
[31] Hock, *Oel u. Kohle* **13**, 697 (1937).
[32] In his first communication, Hock (*Naturwissenschaften* **24**, 159 (1946)) announced the formation of a 50% yield of cyclohexane-1,2-diol, m.p. 104°, but subsequently claimed high yields of the triol. In our repetitions of Hock's experiments, we have always obtained the triol, but never the diol.
[33] Hock and Gänicke, *Ber.* **71**, 1430 (1938).
[34] It may not always be necessary for a hydroperoxide molecule first to decompose to the corresponding oxido compound before it unites with another molecule. A direct route can be simply formulated,

whereby one of the reacting molecules requires as a functional group a double bond, *e.g.*, an olefin, an olefin hydroperoxide, or an unsaturated alcohol, and the other a hydroperoxide group, thus:

$$-C{=}C- + HOOR \rightarrow -C-\dot{C}-\overset{+}{\underset{H}{O}}OR \rightarrow -C(OH)\dot{C}OH.$$

An ether type of dimeride of somewhat variable constitution would still be formed. Since any hydroperoxide molecule formed in the reaction mixture is normally surrounded by many olefin molecules and fewer hydroperoxide molecules or their decomposition products, many "dimeric" molecules of type (XXIII) might well be produced.

[35] Deatherage and Mattill, *Ind. Eng. Chem.* **31**, 1425 (1939).
[36] Hey and Waters, *Chem. Rev.* **21**, 169 (1937).
[37] The peroxidic oxygen content is referred to as P.O.C., and denotes the percentage of oxygen per mol which is contained in (OOH) groups, *i.e.*, twice the percentage of active oxygen per mol. A rapid and convenient method of P.O.C. determination has been devised for use in these investigations by Bolland, Sundralingam, Sutton and Tristram (*Trans. Inst. Rubber Ind.* **16**, 29 (1941)).
[38] Wallach, *Ann.* **365**, 275 (1909).
[39] Dieckmann, *Ber.* **45**, 2704 (1912); Dupont, *Bull. soc. chim. Belgique* **45**, 57 (1936).
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THE COURSE OF AUTOÖXIDATION REACTIONS IN POLYISOPRENES AND ALLIED COMPOUNDS

II. HYDROPEROXIDIC STRUCTURE AND CHAIN SCISSION IN LOW-MOLECULAR POLYISOPRENES *

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One of the most astonishing phenomena connected with the chemistry of rubber is the ease with which it absorbs progressively very small percentages of oxygen, and suffers as a result drastic and progressive reduction of its molecular weight. The natural conclusion to be drawn is that the polyisoprene chains of the rubber are undergoing oxidative scission at one after another of their unsaturated centers, so that the original long hydrocarbon chains become divided into smaller and smaller fragments possessing oxygenated ends. Recent estimates of the molecular weight of rubber by viscosity and osmotic methods range from 240,000 to 360,000 for fractions of decreasing solubility in hydrocarbon solvents[1]. If we accept these figures and assume for the moment that two atoms of oxygen are sufficient to sever the hydrocarbon chains at a double bond, then an absorption of only 0.009–0.013 per cent of oxygen (applied, of course, exclusively to scission reactions) should suffice to reduce the average molecular weight to one-half. If the observed reductions of molecular weight are to be ascribed solely to oxidative scission of the chains, then, provided oxygen-consuming side reactions are few, a fairly exact inverse proportionality may be expected to hold between the uptake of oxygen and the average molecular weight of the degraded rubber. The most striking reductions in the molecular weight per unit of oxygen absorbed must, of course, occur at the very early stages of oxidative fission, while the hydrocarbon chains are still very long, and to be able to follow effectively the quantitative relationship between these important reductions and the oxygen uptake, it is necessary to make experimental provision for the absorption, even distribution, and measurement of very minute quantities of oxygen[2]. Minute though the overall proportion of oxygen necessary to produce a substantial reduction in molecular weight appears in practice to be, however, there is no evidence to indicate that the scission reaction ever follows the course most economical in oxygen, *i.e.*,

$$\cdot CMe{:}CH\cdot + O_2 \rightarrow \cdot COMe + \cdot CHO$$

or indeed represents the sole, or even the most important, line of reaction among the secondary changes which follow the initial peroxidation of the hydrocarbon. The chains of greatly reduced molecular weight are still much too long to permit of any satisfactory direct examination of the individual products for the purpose of confirming the reality of the oxidative scissions or

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of determining the mechanism connecting the initial peroxides with (1) the scission products and (2) other secondary products (if any) comparable with the alcohols, epoxides, ketones, and dimerides formed from cyclohexene and methylcyclohexene[3]. For this reason, the autoöxidative changes occurring in the low-molecular polyisoprenes, dihydromyrcene, dihydrofarnesene, and squalene, have been studied, and the present paper considers especially the character and point of entry of the peroxide groups, the tendency to chain scission, and the formation of oxygenated but unsevered chains.

The formation and character of peroxide groups.—The course of autoöxidative reaction under ultraviolet irradiation which is shown by dihydromyrcene (I), dihydrofarnesene (II), and squalene (III) resembles in its primary aspects

(I) $H\cdot[CH_2\cdot CMe{:}CH\cdot CH_2]_2\cdot H$ $H\cdot[CH_2\cdot CMe{:}CH\cdot CH_2]_3\cdot H$ (II)

(III) $H\cdot[CH_2\cdot CMe{:}CH\cdot CH_2]_3\cdot[CH_2\cdot CH{:}CMe\cdot CH_2]_3\cdot H$

that pursued by various other olefinic substances. The absorbed oxygen forms peroxide groups, and these in lesser or greater degree decay, the peroxidic decompositions occurring side by side with the formation of new peroxide groups, so that the total content of peroxidic oxygen in the reaction mixture tends to fall seriously behind the oxygen intake. Small proportions of oxygen are lost by the formation of carbon dioxide and water, but these losses[4] are not very serious, especially in the early stages of reaction, so the peroxidic oxygen present at any moment represents some fraction, large or small, of the total oxygen in the system. The transformations of the peroxide groups, whether by isomerization or by exercise of their energetic oxidative action on the rest of the molecule (or other molecules), constitute the chief autoöxidative changes.

Now, in all studies of olefinic autoöxidations described in the literature, the reasonably accurate measurement of the peroxide content in the unsaturated molecules and also that of the degree of unsaturation of the highly peroxidic products has been difficult and a source of error. The method of peroxide determination here employed is that referred to in Part I[3], but special care has been necessary to avoid misleading values for the unsaturation of the peroxidized substances. In Figure 1, the peroxide content is plotted against the oxygen content for dihydrofarnesene, dihydromyrcene, and squalene during the early stages of autoöxidation. The behavior of dihydrofarnesene is noteworthy, in that all the absorbed oxygen up to an oxygen intake of 6.0 per cent was found to be peroxidic and the hydrocarbon sustained no serious loss of unsaturation. The reaction mixture, therefore, contained at this point only unchanged hydrocarbon and dihydrofarnesene peroxides, and hence the latter could only have been of the hydroperoxide type. Dihydrofarnesene thus represented a very favorable example for the detailed examination of peroxidic structure, but, owing to the great expense involved in the synthesis of the hydrocarbon (described elsewhere), no further study of the course of reaction could be undertaken. With squalene, absorption of oxygen up to 3.6 per cent was observed. Here, the oxygen absorbed was found to be present entirely in peroxidic form at first, but decay of the peroxide soon set in, and, at the end of the period of observation, only about 57 per cent of that formed had survived. The autoöxidation product consisted of unchanged hydrocarbon, together with considerably oxygenated but largely nonperoxidic substances in which the original unsaturation had become very appreciably diminished. Autoöxidation of dihydromyrcene was carried to an oxygen uptake of 11.6

per cent, and of the peroxide thus formed only 50 per cent survived in peroxidic form at the end of the period; repetitions of the oxidation gave very similar results. Since dihydromyrcene can be prepared with relative ease, it represents a convenient example for study.

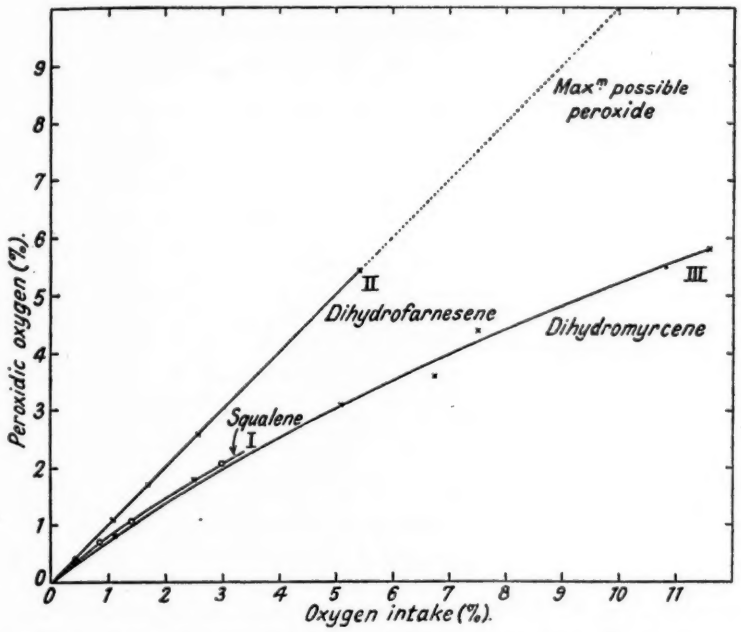

FIG. 1.—Formation of peroxide in dihydrofarnesene, squalene, and dihydromyrcene.

General character of the autoöxidation products.—Pure dihydromyrcene (300 g.) was treated with oxygen in ultraviolet light (temperature 30–40°) for 45 hours, just over 7 per cent by weight of oxygen being absorbed. About two-thirds of the hydrocarbon was found to have escaped oxidation, and of the remaining third, about 4.5 per cent consisted of relatively volatile scission products, and the residue of oxygenated dihydromyrcene possessed an average oxygen content of rather less than 25 per cent (corresponding nearly to $C_{10}H_{18}O_3$). The scission products were distilled below 30° at 0.2 mm. pressure into a liquid-air trap, and the bulk of the unchanged hydrocarbon was driven over below 37° at the same pressure. The oxygenated residue was then fractionated below 70° by evaporative distillation at 10^{-3} mm. in a molecular batch still in an attempt to isolate some of the individual products.

In general the moderate heating (below 45°) in high vacuum caused no very extensive damage to the peroxidized molecules. The peroxide contents of the less volatile portions were consistently high, and the unsaturation was well marked. The active hydrogen values (dependent on both ·OOH and ·OH) were also considerable, and tended to increase from the lower to the higher fractions, although there were considerable fluctuations from fraction to fraction. No satisfactory separation of the individual components of the mixture could. however, be effected. To improve the result if possible, refrac-

tionations of the more volatile distillates were carried out at 0.2 mm. pressure, under a short column. The higher distillation temperatures, however, caused serious secondary change, so adding to the heterogeneity of the substances; and there was unmistakable evidence that very slow oxidative fission was occurring. Catalytic hydrogenation of the most promising fractions, followed by further fractional distillation under a column, did not give a homogeneous product.

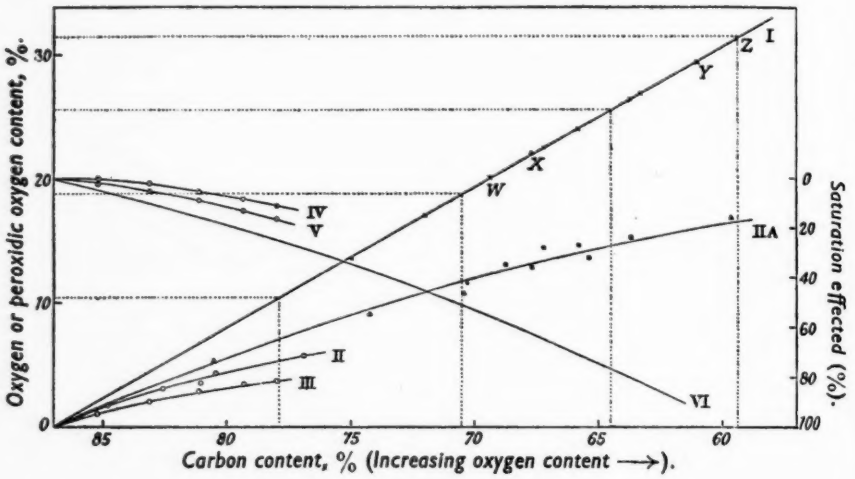

FIG. 2.—Oxidation of dihydromyrcene.

Curve I: Oxygen content of individual distilled fractions (U.H.E.). Curve II: Formation of peroxide in Oxidation No. 1 (U.H.P.). Curve IIA: Approximate peroxide content of the oxygenated hydrocarbon in Oxidation No. 1 (U.H.E.). Curve III: Formation of peroxide in Oxidation No. 2 (U.H.P.). Curve IV: Degree of saturation observed in Oxidation No. 2 (U.H.P.). Curve V: Degree of saturation in Oxidation No. 2 calculated from amount of nonperoxidic oxygen present in the reaction mixture on basis of 1 mol of O_2 per double bond. Curve VI: Degree of saturation in Oxidation No. 2 which should be observed if 1 mol of O_2 added to each double bond (U.H.P.).

[U.H.E. = Unchanged hydrocarbon eliminated from reaction mixture. U.H.P. = Unchanged hydrocarbon present in reaction mixture.]

Figure 2, Curve I, shows the oxygen content, as determined by analysis, of a number of the fractions of undegraded oxygenated dihydromyrcene (selected over the range of oxygenation) plotted against the corresponding carbon content; the points *W*, *X*, *Y*, and *Z* on this curve, however, refer to the higher-boiling fractions of a second batch of oxidized dihydromyrcene. The oxygen values all fall with great precision on the oxygen content-carbon content curve (I) representing the formation of the oxidation stages, $C_{10}H_{18}O$, $C_{10}H_{18}O_2$, $C_{10}H_{18}O_3$, $C_{10}H_{18}O_4$, from the hydrocarbon $C_{10}H_{18}$. All the distillate fractions had remained unpolymerized, and thus each consisted of one or more materials belonging to these[5] oxidation stages, except for the very earliest ones (unrepresented in the diagram), which still contained some unchanged hydrocarbon. It is noteworthy that oxidation can advance as far as $C_{10}H_{18}O_4$ (and indeed the material of fraction *Z* actually had this empirical composition), in spite of the fact that by far the larger proportion of the available hydrocarbon molecules escaped reaction. This very uneven attack of the molecules submitted to the action of oxygen suggests not only that the oxygen enters the chain not less than one molecule at a time, but that the entry of a peroxide group facilitates further attack in the same molecule; moreover, our observa-

tions indicate that such an uneven attack is by no means unusual in the autoöxidative reactions of olefinic substances, and hence it is probable that many statements in the literature purporting to refer to the early stages of oxidation really refer to fairly advanced stages so far as the molecules actually attacked are concerned. Prolonged heating of the peroxidized substances at temperatures above 100° under reduced pressure caused not only redistribution of oxygen, but some (low-molecular) polymerization. Brownish-red, highly oxygenated, thermoplastic solids of trimeric or tetrameric complexity were so obtained.

The growth of peroxide groups in the hydrocarbon chains in comparison with the absorption of oxygen and the corresponding change in the unsaturation of the system deserves comment. The increase in the peroxide content (·O·O·) from stage to stage of a typical oxidation is shown for the undifferentiated mixture of unchanged and oxygenated hydrocarbon in curve II, Figure 2. The same increase, but viewed in relation to just that portion, *i.e.*, about one-third, of the hydrocarbon which ultimately became successfully oxygenated, is shown approximately, for purposes of comparison with the oxygen intake (curve I), in curve IIA. The general level of the peroxide curve, however, varied materially from experiment to experiment in correspondence with small changes in the experimental conditions, and in Figure 2 is shown a second peroxide-content curve (III) at a considerably lower level, that was obtained in a second experiment in which oxidation was accelerated (and the temperature of reaction raised a little) by attaching a reflector to the quartz lamp used previously. The content of nonperoxidic oxygen, obtained by subtracting the ordinates of (II) or of (III) from those of (I), is seen through most of the reaction to amount to a large fraction of the total absorbed oxygen, showing that secondary reaction soon becomes an important feature of the oxidation.

Corresponding to the increasing degree of peroxide decay as the reaction proceeds, there is a progressive diminution in the unsaturation of the system. This diminution is shown for the second of the above experiments, where peroxide decay (see Curve III) was considerably more severe than usual, by Curve IV of Figure 2, and it will be seen that the decrease is small compared with that which would have occurred if the absorbed oxygen had been progressively added at the double bonds (2 atoms per double bond) as represented in Curve VI. The unsaturation of the system cannot, therefore, be affected by the primary oxidation reaction, *i.e.*, peroxidation, and hence the peroxide groups can hardly be other than hydroperoxide groups which, on entering the carbon chain, leave the original double bonds intact. It would be expected, from the evidence of autoöxidative tendencies described in Part I[3], that the degree of double-bond saturation brought about by the oxidation (*cf.* Curve IV) would tend to show a quantitative correspondence with the nonperoxidic oxygen appearing in the reaction, on the basis of two atoms of nonperoxidic oxygen present per double bond lost[6] (Curve V), since the important paths of decomposition open to the hydroperoxide groups all appear to involve concomitant oxidative saturation of a double bond rather than direct disintegration of the groups to leave the double bond intact, *e.g.*, as would occur if the decomposition $:R\cdot CH(OOH)\cdot CH:CH\cdot \rightarrow R\cdot CO\cdot CH:CH\cdot + H_2O$, were involved. The occurrence of advanced stages of oxidation leading to chain scission and beyond would, however, diminish the degree of this correspondence, since peroxidic oxidizing power would then be used for post-saturation purposes. Experimentally, it was found that the degree of saturation effected did not

reach equality with that to be expected on the basis of the nonperoxidic oxygen present, but amounted to about two-thirds of this (see Curve V). Doubtless the appearance of chain-scission products from an early stage of the oxidation adequately accounts for the difference.

The peroxidic constitution.—In the case of peroxidized dihydrofarnesene (above), which suffered over the range of our observation no serious loss of unsaturation, reduction of the peroxide groups present would be expected to lead to the formation of a mixture of hydroxy- and dihydroxydihydrofarnesene [$R{\cdot}OOH + 2H \rightarrow R{\cdot}OH + H_2O$; $R'(OOH)_2 + 4H \rightarrow R'(OH)_2 + 2H_2O$]. If the peroxide groups in oxidized dihydromyrcene are similarly of hydroperoxidic character, as appears from the foregoing evidence to be the case, then those peroxidized molecules which have escaped secondary change, both in the actual oxidation and in any subsequent operations, should yield hydroxy- and dihydroxydihydromyrcenes on reduction, the former doubtless having one or other of the formulas (A), (B), and (C), and the latter one or the other of (D) and (E) (see Part I), or alternatively either compound being a mixture of the appropriate isomerides.

$$CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH(OOH){\cdot}CMe{:}CH{\cdot}CH_3 \rightarrow CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH(OH){\cdot}CMe{:}CH{\cdot}CH_3 \quad (A)$$

$$CH_2(OOH){\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_3 \rightarrow CH_2(OH){\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_3 \quad (B)$$

$$CH_3{\cdot}CMe{:}CH{\cdot}CH(OOH){\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_3 \rightarrow CH_3{\cdot}CMe{:}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_3 \quad (C)$$

$$CH_2(OOH){\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH(OOH){\cdot}CMe{:}CH{\cdot}CH_3 \rightarrow CH_2(OH){\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH(OH){\cdot}CMe{:}CH_2{\cdot}CH_3 \quad (D)$$

$$CH_3{\cdot}CMe{:}CH{\cdot}CH(OOH){\cdot}CH(OOH){\cdot}CMe{:}CH{\cdot}CH_3 \rightarrow CH_3{\cdot}CMe{:}CH{\cdot}CH(OH){\cdot}CH(OH){\cdot}CMe{:}CH{\cdot}CH_3 \quad (E)$$

Since, in all our oxidations of dihydromyrcene, a considerable proportion of the peroxide groups always underwent secondary change during the oxidation itself, it was inevitable that any reduction products of the type (A)–(E), and especially dihydroxy products, such as (D) and (E), would be found in the reduced product mixed with other oxygenated substances of very similar empirical composition. Hence, separation of pure products would be difficult, and the yields of such separated substances poor. In practice, aluminum-amalgam proved to be an effective reducing agent, but the low yield of hydroxydihydromyrcene to be expected was still further diminished, owing to the difficulty experienced in recovering the alcoholic product completely from the alumina formed. Nevertheless, a monohydric alcohol, $C_{10}H_{17}OH$, having two double bonds and one atom of active hydrogen per molecule, was isolated by fractional distillation, and also a corresponding dihydric alcohol, $C_{10}H_{16}(OH)_2$. The former was, with little doubt, (A) or (C), or a mixture of both; the latter, however, on the scale of experimentation open to us, could not be freed entirely from more highly oxygenated substances of similar boiling points, and so the final fractionation product, although showing the correct active hydrogen content, had a somewhat low degree of unsaturation ($\overline{|1.6}$) and a rather too high oxygen content. Repetition of the reduction with a further batch of oxidized dihydromyrcene gave exactly similar results. It is of some interest that the somewhat heterogeneous dihydric alcohol reacted readily and nearly quantitatively with standard lead tetraacetate solution, and hence appears according to Criegee's rule to have consisted almost completely of α-glycols: therefore the major product is likely to have been (E) rather than (D), and

the minor, more highly oxygenated component, a mono-olefinic triol such as

$$CH_3 \cdot CMe(OH) \cdot CH(OH) \cdot CH_2 \cdot CH(OH) \cdot CMe{:}CH \cdot CH_3$$

or

$$CH_3 \cdot CMe{:}CH \cdot CH(OH) \cdot CH_2 \cdot CMe(OH) \cdot CH(OH) \cdot CH_3$$

The products of chain scission.—The observations recorded in Part I indicate clearly that redistribution of the active oxygen of the hydroperoxide groups occurs largely or entirely as the direct result of the energetic oxidizing action of the latter. In the absence of other reactive centers, *e.g.*, $>CO$, $\cdot C(O)C \cdot$, the chief oxidative attack occurs at the olefinic centers, and these accordingly first become saturated by oxygenation and ultimately, if reaction goes far enough, become the seats of chain scission. Two different types of scission reaction are to be distinguished, *viz.*, (1) in which break occurs at the double bond without any oxygenation of the α-carbon atoms, and (2) in which break occurs at the double bond but one or other of the α-carbon atoms becomes oxygenated and subsequently, if reaction goes far enough, split off. The first of these is initiated by an external peroxide or peracid group:

$$R \cdot OOH + \cdot CH_2 \cdot CMe{:}CH \cdot CH_2 \cdot \rightarrow R \cdot OH + \cdot CH_2 \cdot CMe(O) \cdot CH \cdot CH_2 \cdot$$

and the second probably usually, but not necessarily always:

$$\textit{e.g.},\ R \cdot OOH + \cdot CH(OH) \cdot CMe{:}CH \cdot CH_2 \cdot \rightarrow \cdot CMe{:}CH \cdot CH_2 \cdot R \cdot OH + \cdot CH(OH) \cdot CMe(O) \cdot CH \cdot CH_2 \cdot,$$

by an α-situated hydroperoxide group.

All polyisoprene systems in our experience, and notably rubber, appear in the first place to give neutral scission products, and only later are these converted to a serious extent into acidic products containing carboxyl groups. Doubtless for polyisoprenes the neutral products have aldehydic and ketonic ends, and the former can probably absorb oxygen directly under illumination to form peracids and thence carboxylic acids, but it seems likely that the hydroperoxides themselves play a large part in the further oxidation of the scission products:

$$R \cdot OOH + R' \cdot CHO \rightarrow R' \cdot CH(OH) \cdot OOR \rightarrow R' \cdot CO_2H + R \cdot OH$$

The scission products unavoidably formed during the absorption of oxygen by dihydromyrcene contained a good deal of acetaldehyde, acetic acid, and acetone, together with water and some formic acid, showing that scission had occurred at both double bonds of the hydrocarbon, and with little doubt to some extent also at adjacent single bonds. The other degradation products were very mixed and difficult to identify. It is noteworthy, however, that no lævulic aldehyde or acid could be isolated or detected, partly, it is probable, because of its own autoöxidizability, but largely, we believe, because the system $CH_3 \cdot CMe{:}CH \cdot \overset{*}{C}H_2 \cdot \overset{*}{C}H_2 \cdot CMe{:}CH \cdot CH_3$ is most readily attacked, and ultimately becomes most extensively hydroxylated, at one or both of the methylene groups marked *, leading, when the double bonds are severed, to

enolizable ketols or hydroxyaldehydes which are likely to undergo further degradation with rejection of acetic or formic acid.

Autoöxidative scission reactions are of enormous practical significance in connection with the perishing of rubber, the production of rancidity and offensive odors in oils and fat acids, and the production of films from drying oils. It is of interest, therefore, to note that scission of peroxidized dihydromyrcene occurred, not only during the absorption of oxygen by the hydrocarbon and during subsequent heating (in distillation), but also on heating it with water, whereupon volatile products, including acetaldehyde, were formed. It is not impossible that these last fission products are to some extent to be traced to small amounts of ozonide (formed from the ozone usually present in irradiated oxygen) in the oxidation product, but, in view of the observations recorded in Part I[3], it would be expected that heating with water, analogously to heating with dilute sulfuric acid, would serve to cause slow hydrolysis of the hydroperoxide groups and promote oxidative attack at the double bonds.

CONCLUSIONS

(1) The primary reaction involved in the oxidation of polyisoprenes (and probably of all olefinic substances in which the unsaturation is the structural feature which promotes reaction) is the formation of hydroperoxide groups on the α-methylene carbon atoms.

(2) In this primary reaction the unsaturation of the system remains unaffected.

(3) Secondary autoöxidative changes, spontaneous or promoted by heat or other influences, set in with different degrees of facility in different substances and consist largely in the interaction of the hydroperoxide groups at the double bonds, which results mainly in oxidatively saturating the latter without severing them, although in a proportion of molecules reaction goes far enough to cause scission.

(4) In many substances the secondary reactions begin almost at the outset of reaction and proceed side by side with further peroxidation. The entry of oxygen into a molecule appears to facilitate further autoöxidative attack in the same molecule, so that a low overall oxygen intake is compatible with advanced oxidation in some of the molecules.

(5) Reduction of the peroxide groups in those peroxidized dihydromyrcene molecules which have escaped secondary reaction yields alcohols which retain intact the original unsaturation of the hydrocarbon.

(6) Chain scission takes place with some facility at the double bonds, with formation of fragments with oxygenated ends, but subsidiary scission appears to occur also at certain of the single bonds adjacent to the double bonds.

EXPERIMENTAL

Dihydromyrcene.—Myrcene was prepared from bay oil (*Pimenta acris*) by the method of Power and Kleber[7]. The well-washed hydrocarbon, fractionated over sodium, had b.p. 51–53°/10 mm., $d_4^{20°}$ 0.7981, $n_D^{22°}$ 1.468, and gave at once with maleic anhydride the adduct, m.p. 34° (Diels, m.p. 34–35°), and the latter, by hydrolysis, the corresponding dicarboxylic acid, m.p. 122° (Diels, m.p. 122–123°). Yield, 20% of original oil. The myrcene was reduced with sodium and alcohol, as described by Semmler and Mayer[8], except that 162 g. of sodium and a total of 1820 cc. of absolute alcohol per 500 g. of hydrocarbon sufficed to ensure complete reduction. The well-washed hydrocarbon, after

being twice distilled over sodium through a Widmer column, boiled at 52.5–55°/11 mm. (found: C, 86.8; H, 13.1; calculated for $C_{10}H_{18}$: C, 86.9; H, 13.1%). It had $d_{4^\circ}^{20^\circ}$ 0.7809, $n_D^{23^\circ}$ 1.4495, and gave a tetrabromide, m.p. 87–88° (found: Br, 69.8; calculated: Br, 69.8%). Semmler and Mayer report $d_{4^\circ}^{15^\circ}$ 0.7802, $n_D^{20^\circ}$ 1.4507 and m.p. of tetrabromide, 87°. To ensure that the dihydromyrcene contained no myrcene, a portion (10 g.) was heated at 100° for 10 minutes with maleic anhydride. No visible reaction occurred, no trace of adduct could be found, and the recovered hydrocarbon had the original physical constants.

Squalene.—A fraction of the liver oil of *Symnorhinus lichia* of b.p. 225–235°/1 mm. was used, after it had been well washed with caustic alkali and with water. This pale yellow hydrocarbon contained oxygenated impurities, as Heilbron *et al.*[9] had observed with similar specimens, but these were expeditiously and satisfactorily removed by adsorption on activated alumina (21 g. of hydrocarbon dissolved in 1000 cc. of light petroleum run slowly through a column of alumina 33 cm. × 2 cm., and the chromatogram developed by 150 cc. of light petroleum). The purified oil (found: C, 87.8; H, 12.3; calculated for $C_{30}H_{50}$: C, 87.7; H, 12.3%) had $d_{4^\circ}^{20^\circ}$ 0.8562, $n_D^{23^\circ}$ 1.494 $[R_L]_D$ 139.5, and showed like Heilbron's product an appreciable molecular exaltation (1.5 units). The cause of this exaltation will be considered in a later paper.

Dihydrofarnesene.—This triisoprene was synthesized from geraniol, as will be described later.

Determination of Unsaturation.—For the determination of unsaturation in oxidized polyisoprenes, the iodine-value method is convenient, but has the disadvantage that organic peroxides react with the potassium iodide used as reagent, and by liberating iodine cause low unsaturation values to be obtained. Direct hydrogenation is an alternative but, owing to the necessity of determining the peroxide content separately and subtracting the hydrogen equivalent of the peroxide ($R \cdot OOH + H_2 \rightarrow R \cdot OH + H_2O$) from the total quantity of hydrogen absorbed, the method is subject to a double error, which renders it too inaccurate for use with small quantities of material, although it enables very useful near approximations to be made with specimens of several grams or more. Determination of unsaturation by bromine addition has proved unsatisfactory, and determination by means of standard solutions of peracids is unsuitable, owing to the tendency of these oxidizing agents to cause chain scission, with consumption of additional peroxide. Of all these methods, as conducted under various recommended procedures, the iodine value has proved to be most satisfactory for general analytical control, but the magnitude of the error even under standard conditions of working is variable, owing to differences in the reducibility of different peroxides. For the reactive hydroperoxides of low-molecular polyisoprenes and cyclohexene peroxides, unsaturation values found by the iodine value method are estimated to be 4–5% too low, but not more, provided the final titration after the addition of potassium iodide be conducted rapidly, and in a solution well diluted with water. The existence of this error renders the direct observation of very small changes in unsaturation in the early stages of peroxidation, *e.g.*, in the case of dihydrofarnesene, unreliable. The unsaturation values used in plotting Curves (IV)–(VI), Figure 2, are uncorrected ones, and hence the degrees of saturation there shown are considered to be about 5% higher than the actual value.

General oxidation procedure.—The unsaturated hydrocarbon, together with a diluent if desired, was placed in a 2-necked Pyrex flask, and connected through a calcium chloride tube to a gas burette and reservoir containing oxygen. The air in the flask was displaced with oxygen, and the flask placed 15 cm.

from an ultraviolet lamp (Hanovia U.V.S. 500), and shaken mechanically. The heat radiated from the lamp kept the flask at a temperature between 35° and 40°. Usually after an induction period of about 1 hour, absorption of oxygen began, and was allowed to proceed until the desired amount of oxygen had been absorbed, or until absorption seriously slackened. For determination of the peroxide formed, or the saturation effected from stage to stage in the oxidation, suitable portions of material were withdrawn with a pipette through one of the necks of the flask, the level of the gas burette being noted before and after the interruption, and the air unavoidably admitted to the flask during the interruption being replaced by oxygen before oxidation was continued. Invariably in the course of the oxidation, a little water was eliminated, and some carbon dioxide formed. Since neither of these up to the point of oxidation desired interfered with the absorption of oxygen or caused any very serious error in the measurement of the oxygen intake (as confirmed by numerous comparisons of the latter with the oxygen content of the products), no steps were taken to remove them as they were formed.

Oxidation of squalene.—The purified squalene (10 cc.; 8.45 g.), dissolved in 100 cc. of pure dry benzene, was oxidized at 35–40° for 105 minutes after the induction period (60 minutes) had ended. Withdrawals of 2 cc. of the solution were made from time to time, and the peroxide content of each sample determined. The change in the peroxide content of the solution of hydrocarbon up to an average oxygen intake of 3.6% of its weight is shown in Figure 1 (Curve I). The product was freed from solvent by distillation of the latter at reduced pressure, and the residual oil (7.6 g.) was divided into two parts by fractional dissolution in methyl alcohol. The alcohol-insoluble portion (5.5 g.) was nearly free from oxygen [found: C, 87.2; H, 12.3; O (by difference), 0.5; calculated for $C_{30}H_{50}$: C, 87.7; H, 12.3%] and consisted mainly of unchanged squalene, while the alcohol-soluble portion consisted of oxygenated squalene having an average empirical composition of $C_{30}H_{50}O_{3.65}$, and a peroxide content (6.5%) slightly more than one-half the total average oxygen content.

Oxidation of Dihydrofarnesene.—This triene hydrocarbon (4.14 g.) was oxidized without a diluent, withdrawals of samples (3) being made at intervals as before. The hydrocarbon, which had been kept in a stoppered bottle for 1 week after purification, contained at the outset 0.22% of peroxidic oxygen, and finally after absorption of 6.0% of its weight of oxygen (leading to an average empirical formula of $C_{15}H_{26}O_{0.82}$) contained 6.0% of peroxidic oxygen. The unsaturation, determined by iodine values, diminished inappreciably, and had finally decreased by 4.8% (<0.8% corrected) of the initial figure.

Oxidation of Dihydromyrcene.—Dihydromyrcene (100 g.) was oxidized without a diluent during 42.5 hours, samples being withdrawn at intervals for peroxide determination. The total oxygen intake amounted to 11.6% of the weight of hydrocarbon taken. The variation of the peroxide content as the absorption of oxygen proceeded is shown in Figure 1 (Curve III).

A further quantity of hydrocarbon (300 g.) was oxidized as before, absorption of oxygen being continued until it became slow. A total of 16,550 cc. of oxygen was absorbed in 45 hours. The product (nearly 323 g.) was placed in a 2-necked flask, surmounted by a Widmer column and connected to a liquid-air trap. The flask was very gently warmed at 0.2 mm. pressure to drive over (1) very volatile products (*A*) which collected in the liquid-air trap (27.6 g.), (2) volatile substances (*B*) of b.p. 30–37° (205 g.), leaving (3) a residue (*C*) (85 g.) in the flask.

The fraction (*A*) evolved no gases when it was warmed slowly up to 10°, and it could be distilled at atmospheric pressure under a short Vigreux column without great loss of volatile substances. There were obtained (1) acetaldehyde (dimedon derivative, m.p. 140–141°; mixed m.p. 140–141°; found: C, 70.5; H, 8.5; calculated for $C_{18}H_{26}O_4$: C, 70.55; H, 8.55%); (2) a volatile liquid, b.p. 30–74°, which yielded on refractionation more acetaldehyde, a quantity of acetone (2,4-dinitrophenylhydrazone, m.p. 126°; mixed m.p. 126°; found: N, 23.9; calculated for $C_9H_{10}O_4N_4$: N, 23.5%); (3) a fraction, b.p. 60–90°, which separated into two layers and on refractionation gave water, some acetic acid (*p*-bromophenacyl ester, m.p. 84°; mixed m.p. 85°; found: C, 46.35; H, 3.6; Br, 31.65; calculated for $C_{10}H_9O_3Br$: C, 46.7; H, 3.5; Br, 31.1%), a small amount of pungent volatile acid of b.p. approx. 100°, which satisfied Rimini's and other qualitative tests for formic acid, and a quantity of unidentified volatile liquid substance, and (4) 22 g. of crude hydrocarbon [added to (*B*)]. The total yield of the volatile scission products including acetaldehyde, acetic acid, water, and acetone and unidentified products amounted to 4.5–8% of the weight of hydrocarbon actually oxygenated (approx. 100 g.).

The fraction (*B*) (205 g. + 22 g.) was found on refractionation to consist almost entirely of unchanged dihydromyrcene, but it contained some nonketonic oxygenated material. The total proportion of unchanged dihydromyrcene, including the first of the subfractions of (*C*, I) (see below) was estimated to be 200 g.

The fraction (*C*) was a light yellow, fairly mobile oil, of strong peroxidic character (peroxidic oxygen, 9.62%), which was first partly distilled at 10^{-3} mm. pressure in a batch still, the most volatile portion, (*C*, I) (16.65 g.; peroxidic oxygen, 0.94%), being collected in a liquid-air trap, the intermediate portion (*C*, II) (29.7 g.; peroxidic oxygen, 12.9%) distilling at 60–70° as a slightly viscous, yellowish oil, leaving a residue (*C*, III) (25.85 g.; peroxidic oxygen, 12.2%) of yellow viscous liquid.

The fraction (*C*, I) was divided by fractional distillation under a short column into 5 fractions ranging in b.p. from 56° to 104°/12 mm. The first (2 g.) consisted of dihydromyrcene, the second, containing only 6.05% of oxygen, was of rather lower unsaturation than dihydromyrcene (179.8 g. equiv. to 2 I_2) and consisted of dihydromyrcene mixed with an oxygenated substance which appeared to be an alcohol (? tertiary) since it reacted with 3,5-dinitrobenzoyl chloride to give a red oil, which in turn gave a thick red oil with α-naphthylamine. The third was acidic, containing a little formic acid which had been produced by thermal degradation during the distillation; when the formic acid was removed, the highly oxygenated residue had barely one-half the unsaturation of dihydromyrcene (148.6 g. equiv. to I_2) and was nonketonic [found: C, 75.0; H, 11.55; O (by difference), 13.45%]. The fourth fraction was also nonketonic, but was more highly oxygenated than the third and slightly more unsaturated [found: C, 72.0, 72.05; H, 10.65, 10.9; O (by difference), 17.35, 17.05%; 138.7 g. equiv. to I_2]. The fifth (1.1 g.), which was very viscous, and apparently somewhat polymerized by heat, was discarded.

A portion (18 g.) of the fraction (*C*, II) was divided by fractional distillation at 10^{-3} mm. pressure in the batch still into five portions (*C*, II, *a–e*), four of which were distillates ranging in b.p. from 40° to 50°, and the fifth the residue. The following data were obtained: *C*, II*a*: C, 65.85; H, 9.85; O (by difference), 24.3; O (peroxidic), 11.7; active H, 0.62%; *C*, II*b*: O (peroxidic), 11.7%; *C*, II*c*: C, 67.2; H, 10.2; O (by difference), 22.6; O (peroxidic), 14.6; active H, 0.74%; *C*, II*d*: C, 63.7; H, 9.8; O (by difference), 26.5; O (peroxidic),

15.5%; *C*, IIe: C, 63.65; H, 9.5; O (by difference), 26.85%. A little volatile material (1.2 g.) of low peroxidic content (1.6%) also collected in the liquid-air trap.

Of the above fractions *C*, IIc was reduced catalytically by means of Adams's catalyst, which was removed by centrifuging. The saturated and peroxide-free product was divided by fractional distillation into 6 fractions. Of these (1), b.p. 82–85°/12 mm. (0.15 g.), closely resembled (2) and was not separately examined; (2) was a sweet-smelling oil, b.p. 86–90°/12 mm. (found: C, 73.0; H, 12.95%), which reacted with 3,5-dinitrobenzoyl chloride to give a red oil, but this gave no solid adduct with α-naphthylamine[10]; (3) was a nearly odorless oil, b.p. 96–98°/12 mm. [found: C, 72.6; H, 12.7; O (by difference), 14.7%], which probably contained as minor component an alcohol of formula $C_{10}H_{22}O$, since it reacted with 3,5-dinitrobenzoyl chloride to give a red oil, forming with α-naphthylamine a somewhat unstable and difficultly crystallizable *derivative*, m.p. 91–96° (15% yield) (found: N, 8.8; $C_{17}H_{24}O_6N_2$, $C_{10}H_9N$ requires N, 8.9%), but since its oxygen content greatly exceeds that of hydroxydihydromyrcene (O, 10.4%) which has approximately the same b.p., the major component must contain, together with hydroxyl, a volatile oxygen-containing group such as epoxy; (4) was an odorless oil, b.p. 104–114°/12 mm. (found: C, 70.95; H, 11.95%); (5) was a viscous oil, b.p. 117–122°/12 mm., of high oxygen content and hydroxylic character which probably consisted mainly of dihydric alcohol, $C_{10}H_{22}O_2$, and in part of an α-glycol, since about one-half reacted with lead tetraacetate (found: C, 68.4; H, 11.55; calculated for $C_{10}H_{22}O_2$: C, 68.96; H, 12.6%).

The residue (*C*, III) remaining in the still was a pale yellow syrup of average composition $C_{10}H_{18}O_{3.2}$ and peroxide content 12.2%, *i.e.*, an average of 0.71 ·OOH group per mol. A portion (14.3 g.) was hydrogenated in presence of Adams's catalyst, and the saturated hydroxylic products were divided into ten portions by fractional distillation, leaving a tiny residue. All fractions were yellow oils, and the 4 lowest ones, b.p. 40–110°/10 mm., resembled those derived by hydrogenation of fraction (*C*, IIc) above; the higher ones, *C*, III, b.p. 75–146°/1 mm., all had the empirical composition $C_{10}H_{19.8}O_{2.5}$, and the highest (*C*, III) and the residue had the composition $C_{10}H_{18.5}O_{2.3}$ and $C_{10}H_{17.5}O_{2.26}$, respectively. It is to be deduced, therefore, that the high subfractions have taken up an average of 1.8 atoms of hydrogen and lost 0.7 atom of oxygen per mol, and hence the peroxidic parent substance must have contained an average of 0.9 and approx. 0.7 ·OOH group per mol. The final two fractions (one of which was the residue), however, have respectively gained $H_{0.5}$ and lost $H_{0.5}$ per mol, and respectively lost $O_{1.0}$ and $O_{0.95}$ per mol. This doubtless marks the beginnings of the post-saturation autoöxidative changes leading to chain scission and its accompaniments of water and carbon dioxide elimination, and in the residue possibly of polymerization.

Advanced stage of oxidation.—Oxidation of 100 g. of dihydromyrcene gave, after exhaustive distillation of the less oxygenated fractions at reduced pressures and at bath temperatures below 100°, a residue in the still having a composition nearly $C_{10}H_{18}O_4$ and containing 11% of peroxidic oxygen [found: C, 59.7; H, 9.0; O (by difference), 31.3. $C_{10}H_{18}O_4$ requires C, 59.4; H, 9.0; O, 31.6%]. In another oxidation of hydrocarbon the final fraction obtained by distillation had an empirical formula of nearly $C_{10}H_{18}O_{3.7}$ [found: C, 61.0; H, 9.1; O (by difference), 29.9%] and peroxidic oxygen 15.1%.

Action of prolonged heating.—The oxidation product from 29 g. of dihydromyrcene (7.1% oxygen intake) was freed from unchanged hydrocarbon, and

fractionally distilled at successive pressures of 13 mm., 1–2 mm., and 10^{-3} mm., the temperature of the heating bath being allowed to rise to about 150° in each case. The residue in the still (approx. 5 g.) formed a brownish-red, resinous mass, which was extensible on warming, and able to yield fine threads. It had approximately the composition $C_{10}H_{18}O_2$, and from cryoscopic determinations had between tri- and tetrameric complexity [found: C, 70.2; H, 9.3; O (by difference), 20.5%; *M* (in benzene), 610; $C_{10}H_{18}O_2$ requires C, 70.6; H, 10.6; O, 18.8%; *M*, 170]. The polymerization process had thus involved material loss of both hydrogen and oxygen, probably largely as water.

Reduction of hydroperoxido- and dihydroperoxidodihydromyrcene.—Dihydromyrcene (300 g.) was oxidized in a quartz flask to an oxygen intake of only 1%, and then immediately reduced by aluminum-amalgam in moist ether containing a little alcohol. Reaction was vigorous at first and, after 24 hours, all peroxidic material had disappeared. The ethereal solution, freed from alumina and from the large bulk of unchanged dihydromyrcene, gave only a moderate yield of reduced product, which by reextraction of the alumina was finally raised to 60% of that expected. Since extensive secondary autoöxidation processes unavoidably accompany peroxidation, it was necessary to select the desired products by careful fractional distillation. Fractions were finally obtained of b.p. (1) 55–58°/12 mm. (1.7 g.), (2) 58–83°/12 mm. (0.9 g.), (3) 90–103°/12 mm. or 70–76°/1 mm. (1.8 g.), (4) 80–96°/1 mm. (0.1 g.), (5) 96–106°/1 mm. (0.5 g.), (6) 115°/1 mm. (0.5 g.), and (7) residue (1 g.). Fractions (1) and (2) both contained some dihydromyrcene, but (3) was free from hydrocarbon and had the correct composition and characteristics for *hydroxydihydromyrcene* (found: C, 77.75; H, 11.35; active H, 0.65; $|\overline{\overline{1.95}}$; $C_{10}H_{18}O$ requires C, 77.9; H, 11.7; active H, 0.65%; $|\overline{\overline{2.0}}$). The alcohol reacted with 3,5-dinitrobenzoyl chloride to give a thick red oil, affording a noncrystalline complex with α-naphthylamine.

Fraction (3) approximated in composition and characteristics to *dihydroxydihydromyrcene* (found: C, 68.85; H, 10.45; active H, 1.05; $|\overline{\overline{1.6}}$. $C_{10}H_{18}O_2$ requires C, 70.6; H, 10.6; active H, 1.18%; $|\overline{\overline{2.0}}$), but clearly contained a little more highly oxygenated substance. The diol reacted with 0.1 *N* lead tetraacetate (consumption: 96.5% of theory) and probably consists mainly of a 1,2-diol of formula (E).

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[3] See preceding paper in this January **1943** issue of RUBBER CHEMISTRY AND TECHNOLOGY.
[4] Discussion of the significance of these is postponed, but, owing to their low value the oxygen intake does not differ materially from the oxygen content as determined by analysis up to an advanced stage of reaction.
[5] Whether or not any oxygenated derivatives containing odd numbers of oxygen atoms are present must depend on the occurrence or otherwise of intermolecular reactions, such as $ROOH + —C:C— \rightarrow ROH + —\underset{\diagdown\,\diagup}{\overset{|}{C}}—\underset{|}{C}—\underset{O}{}$, and $R(OOH)_2 + —C:C— \rightarrow R(OH)OOH + —\underset{\diagdown\,\diagup}{\overset{|}{C}}—\underset{|}{C}—\underset{O}{}$.
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VISCOSITY AND CRYOSCOPIC DATA ON POLYSTYRENE

DISCUSSION OF STAUDINGER'S VISCOSITY RULE*

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Although polystyrene has been known for about a century[1], it was not until recently that its use as a commercial molding plastic and electrical insulation became important.

Since the physical properties of polystyrene depend on its state of polymerization, it is desirable to have some reliable method to determine average molecular weights of different preparations, as well as of fractions which may be separated from them to determine polymer size distribution.

Staudinger[2] and his students carried out extensive investigations of polystyrene in an attempt to show some constant relation between viscosity, concentration, and molecular weight. These results were not conclusive, since variations in the Staudinger K_m value ranged from 7.4×10^{-4} to 1.7×10^{-4} in the polymeric range of average molecular weights from 500 to 13,000, respectively.

When viscosity and osmotic molecular weight data were employed in the case of more highly polymerized styrene fractions, Staudinger[3] obtained K_m values ranging from about 1.2×10^{-4} to 0.4×10^{-4} as the temperature of polymerization increased from 20° to 200° C. The explanation offered for this decrease in K_m value with temperature was that branch chaining occurs as the result of increasing the temperature of polymerization. The effect of variations in polymer size distribution under different conditions of polymerization might also be used to explain these changes.

Similar studies[4] of polyindene and hydrogenated polyindene, ranging in molecular weight from 570 to 6000, led to K_m values from 12×10^{-4} to 1.6×10^{-4}, respectively. From these results, Staudinger selected a K_m value of 1.8×10^{-4} to calculate the average molecular weight of both polystyrene and polyindene by measuring the viscosity of their solutions in benzene or Tetralin, using his well-known equation:

$$M = \frac{\eta_{sp}}{C \times K_m} \qquad (1)$$

The unsatisfactory nature of these and similar results on other polymers has been the basis for frequent adverse comment on the Staudinger viscosity method of determining molecular weights. In fact, several investigators, including Staudinger, have recently placed increased emphasis on the osmotic method, since they are of the opinion that osmotic molecular weights are generally more reliable than those obtained from viscosity measurements, especially when applied to nonlinear polymers. One cannot subscribe to this view, however, in the case of linear polymers, since numerous variables in the

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viscosity method have recently been cleared up[4], and the more reliable viscosity-molecular weight equation:

$$M = \frac{\log \eta_r \times K_{cm}}{C} \tag{2}$$

based on the Arrhenius relation:

$$\frac{\log \eta_r}{C} = K_c$$

has been adopted. Furthermore, it is clear that the failure of solutions of high-molecular-weight polymers to obey Raoult's law results in osmotic molecular weight values which are inordinately high. For example, Staudinger and Fischer[11] obtained the value of 105,000 for the osmotic molecular weight of gutta-percha hydrocarbon in toluene. Their viscosity data, using the recently determined K_{cm} value[5] of 0.75×10^{-4}, give an average molecular weight of 44,000, which checks our recent value for the same substance[6]. We have shown that gutta has a very narrow polymer size distribution; therefore, the values by the two methods can be compared directly.

Values of 300,000 to 500,000 are usually reported for the osmotic molecular weight of crepe rubber in benzene or toluene, whereas the viscosity method gives a value of about 105,000 if based on the whole rubber[6]. The same situation exists in the case of other high polymers of the straight-chain type.

Staudinger selected K_m for polystyrene of 1.8×10^{-4}, based on cryoscopic measurements on polymers ranging in molecular weight from 7000 to 13,000. It appears from our work on polyprenes[5] and polyisobutylene[7] that cryoscopic values for these polymers are likely to be too high, due to the probable failure of solutions of polystyrene in this molecular weight range to obey Raoult's law.

Since Equation 2 will be used in the present investigation, the K_{cm} values have been calculated from Staudinger's data for polystyrene in benzene, and found to range from 0.34×10^4 to 1.46×10^4 for molecular weights ranging from 500 to 13,000, respectively; the K_{cm} for the previously mentioned indene polymers in benzene range from about 0.30×10^4 to 1.6×10^4.

The authors' recent work[5] showed that the high K_{cm} value largely reflects the deviations in the cryoscopic measurements with concentration, in the case of polymers with chain lengths exceeding those which form ideal solutions. For example, in the case of a polyprene fraction, a cryoscopic molecular weight of 6000 was obtained at 9 per cent concentration, whereas at the usual 2 per cent concentration employed by Staudinger, the value was 14,300. It is then readily seen that K_{cm}, which is equal to $M \div (\log \eta_r/C)$, becomes inordinately high when it is based on such cryoscopic measurements, made at concentrations employed by Staudinger and his students. Since K_m is calculated from $(\eta_{sp}/C) \div M$, it is also seen why it is too low when obtained in this fashion.

In view of this situation, the present investigation was undertaken to establish more reliable K_{cm} values for polystyrene and polyindene and to determine the limit of molecular weight of polystyrene within which its solutions obey Raoult's law. Solvent effects and fractionation methods also constituted a part of this investigation. Only highly fractionated polymers were employed to determine the K_{cm} value on account of the large effect of polymer size distribution on cryoscopic results.

MATERIALS

The starting polystyrene material, A, was a liquid polymer obtained by catalytic polymerization; fractionation indicated that A consists largely of a mixture of polymers ranging in molecular weight from about 300 to 1200. Data regarding the preparation and properties of various fractions prepared from this material are given in Table I.

TABLE I

FRACTIONS FROM LIQUID POLYSTYRENE

Polymer	Percentage of original material	$\frac{\text{Log } \eta_r}{C}$ in benzene	Cryoscopic mol. wt. in benzene	Method of preparation
A liquid	100	0.127	...	Catalytic polymerization followed by vacuum distn. at 170° C, to remove monomer and dimer.
A_1 liquid	14.6	0.093	292	Second cold CH_3OH ext. from A.
A_2 liquid	17.0	0.097	344	A dissolved in acetone, CH_3OH added; filtrate decanted from ppt., evapd., washed with cold CH_3OH.
A_3 liquid	12.7	0.105	386	A_2 rewashed with cold CH_3OH.
A_4 solid	20	0.142	608	32% removed from A by cold CH_3OH extn.; residue dissolved in acetone, partially pptd. with CH_3OH; ppt. discarded; A_4 pptd. by addition of more CH_3OH.
A_5 solid	6	0.278	1200	A dissolved in acetone; higher polymer fraction pptd. with CH_3OH; ppt. redissolved in acetone; A_5 pptd. on addition of CH_3OH.

The polystyrenes shown in Table I represent special fractions derived from liquid polystyrene A and therefore do not give complete distribution data, as all of the material is not represented. The dimer content of A_1 was reduced to a small proportion by discarding the first alcohol extract, leaving A_1 containing largely trimer. A_2 and A_3 represent trimer preparations containing increasing amounts of tetramer. In the case of A_4 a very narrow fraction was obtained by first removing the dimer and trimer by cold alcohol extraction and then separating an intermediate fraction, A_4, by fractional precipitation, which was designed to leave tetramer and pentamer in solution. The method of preparation and low percentage of A_5 indicate that it has very narrow distribution of polymer size.

The present investigation indicates that material A consists largely of a mixture of polystyrene homologs in the range of two to twelve styrene molecules.

Material B_4 is the second hot acetone extract, which followed two cold acetone extractions of a commercial low-molecular-weight polystyrene B_1. Some data on these extracts follow:

Material	$\frac{\text{Log } \eta_r}{C}$ in benzene
Commercial material B	3.01
B_2 (2nd cold acetone extract of B_1, 2% extract)	0.354
B_4 (2nd hot acetone extract from B_2 residue, 3.5% extract)	0.546

All materials were heated under high vacuum at 100° C to constant weight to remove the last traces of solvent. In the case of fractions A_1, A_2, and A_3, heating was at 80° C until the loss in weight was at a constant rate, since these polymers had appreciable vapor pressures.

Hydrogenated polyindene fractions.—A colorless clear hydrogenated polyindene resin obtained from the Neville Company was fractionated, with the results shown in Table II. A small amount of hydrogenated polycoumarin is present, which cannot be over about 8 per cent, judged by the analysis given in Table II. The presence of hydrogenated polycoumarin should have practically no effect on the value of K_{cm}.

TABLE II

FRACTIONATION OF HYDROGENATED POLYINDENE RESIN

Fraction no.	Percentage of original material	Treatment	$\frac{\text{Log } \eta_r}{C}$ in benzene
Original	100	.....	0.134
I	2.0	Cold alcohol ext. (3 extns.)	0.105
II	64.6[a]	Residue from I dissolved in C_6H_6; fraction III separated by pptn. with alcohol	0.128
III	33.4[a]	Precipitate from I	0.172

ANALYSIS

	C	H	O by difference	Ratio, H/C
Found fraction II	87.46	11.37	1.17	1.55
Found fraction III	87.78	11.15	1.07	1.53
Theory for $(C_9H_{14})_n$	88.44	11.56	...	1.55

[a] Heated to constant weight at 150° C under vacuum before using in cryoscopic and viscosity measurements.

DETERMINATION OF K_{cm}

The viscosity and cryoscopic data for all polystyrene and polyindene fractions are given in Table III. The cryoscopic data for polystyrene fraction at different concentrations in benzene are plotted in Figure 1. Deviation from Raoult's law is appreciable in the case of polystyrene fraction A_5, having a molecular weight somewhat in excess of 1000 and corresponding to a polymer chain of about twenty carbon atoms, or one-fourth the chain length causing deviation in the case of polyprene[5] and polyisobutylene[6]. Cryoscopic measurements of polymer fraction B_4 were unsatisfactory when made in the usual manner, since crystallization following supercooling resulted in a temperature of more than 2° C above the freezing point of pure benzene. This also occurred in the case of polyisobutylene polymer having a molecular weight of about 5000[6]. Possible formation of a polymer-benzene complex may explain this phenomenon. Although the cryoscopic measurements in cyclohexane of fraction B_4 did not show this effect, there was a slight precipitation of the polymer on cooling which may have influenced the results. The cryoscopic measurements on benzene solutions of polyindene behaved normally; and there appears to be no deviation in Raoult's law in this case up to a molecular weight of about 1200, which was the highest polymer studied.

It is of interest to note that the K_{cm} values of the lower polystyrene polymers agree with similar data published by Staudinger[2] who obtained values for K_{cm} of 0.34×10^4 to 0.43×10^4 for polymer fractions ranging in molecular weight from 438 to 595.

The data in Table III are plotted in Figure 2 to show the molecular weight dependency of polystyrene fractions A_1 to A_5, inclusive.

TABLE III

VISCOSITY–MOLECULAR WEIGHT OF POLYSTYRENE AND POLYINDENE FRACTIONS

Solvent	Concentration: Base molal	Concentration: g./100 g. solvent	η_r	$\frac{\text{Log } \eta_r}{C}$	$\Delta_1° - \Delta_2°$	Cryoscopic mol. wt.	$K_{em} \times 10^{-4}$
			Polystyrene fraction A_1				
C_6H_6	0.080	0.95	...	...	0.166	293	0.32
	0.159	1.92	...	...	0.333	295	0.32
	0.318	3.90	1.072	0.094	0.686	291	0.31
	0.636	8.06	1.145	0.092	1.426	290	0.31
			Polystyrene fraction A_2				
C_6H_6	0.079	0.94	...	...	0.137	352	0.36
	0.158	1.89	...	...	0.277	349	0.36
	0.315	3.86	1.072	0.096	0.582	338	0.35
	0.630	8.00	1.151	0.098	1.212	337	0.34
			Polystyrene fraction A_3				
C_6H_6	0.080	0.95	...	...	0.124	393	0.38
	0.159	1.92	...	...	0.260	379	0.36
	0.318	3.90	1.079	0.104	0.516	387	0.37
	0.636	8.06	1.167	0.105	1.069	386	0.37
			Polystyrene fraction A_4				
C_6H_6	0.080	0.95	...	...	0.083	585	0.41
	0.160	1.92	...	...	0.160	615	0.43
	0.320	3.90	1.107	0.138	0.320	623	0.45
	0.640	8.06	1.240	0.146	0.681	607	0.42
C_6H_{12}	0.070	0.94	...	...	0.301	633	0.44
	0.140	1.89	...	...	0.594	644	0.45
	0.279	3.85	1.095	0.141	1.184	660	0.47
	0.558	7.90	1.211	0.148	2.287	698	0.47
			Polystyrene fraction A_5				
C_6H_6	0.097	1.17	1.058	0.254	0.046	1300	0.51
	0.194	2.35	1.123	0.260	0.099	1220	0.47
	0.387	4.76	1.279	0.276	0.212	1150	0.42
	0.774	9.92	1.649	0.280	0.471	1080	0.39
			Polystyrene fraction B_4				
C_6H_6	0.080	0.94	1.105	0.546	0.015	3200[a]	0.59
	0.159	1.91	1.216	0.533	0.033	2960	0.56
	0.317	3.88	1.475	0.531	0.076	2610	0.49
	0.634	8.03	2.148	0.524	0.178	2310	0.44
C_6H_{12}	0.070	0.94	...	...	0.067	2830[b]	0.53[c]
	0.139	1.89	1.130	0.380	0.129	2960	0.56
	0.273	3.85	1.307	0.430	0.271	2870	0.54
	0.555	7.90	1.772	0.446	0.504	3160	0.59
			Hydrogenated polyindene fraction II				
C_6H_6	...	1.17	...	...	0.089	672	0.50
	0.327	...	1.109	0.137	...	...	...
	0.654	10.50	1.247	0.146	0.716	750	0.51
			Hydrogenated polyindene fraction III				
C_6H_6	...	1.15	...	...	0.052	1130	0.60
	...	2.32	...	...	0.100	1190	0.63
	0.321	...	1.143	0.181	...	...	...
	0.642	9.84	1.341	0.199	0.408	1240	0.63

[a] Anomalous behavior; separate determinations varied as much as ± 15%. Results are average of several determinations.
[b] Solutions showed slight precipitation on cooling.
[c] Using average value for log η_r/C of C_6H_6 solutions.

Staudinger[2] accounted for the large deviations in the K_m values between the lower and higher styrene polymers by the supposition that an increase in chain length resulted from the end phenyl group standing out in the direction of the chain, which increased the chain length by two benzene rings. It

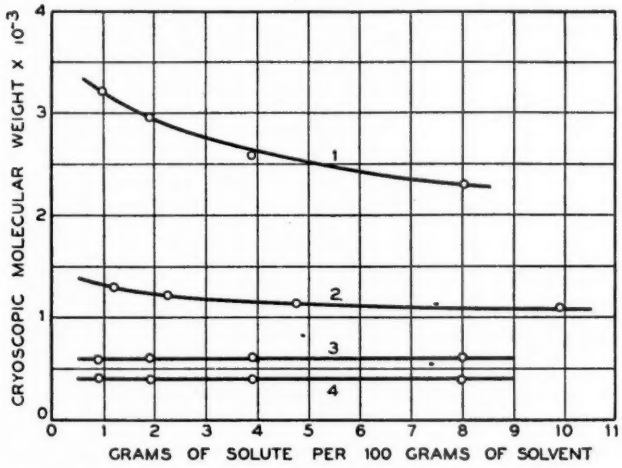

FIG. 1.—Effect of concentration on cryoscopic molecular weight of polystyrene fractions in benzene.
1. Fraction B_4
2. Fraction A_5
3. Fraction A_4
4. Fraction A

appears, however, from present data on the effect of chain length on K_{cm} that this explanation of the increase in K_{cm} with molecular weight cannot be correct, since the chain length of a trimer so constituted would be more than twice that of a normal trimer where the phenyl groups stand out from the sides of

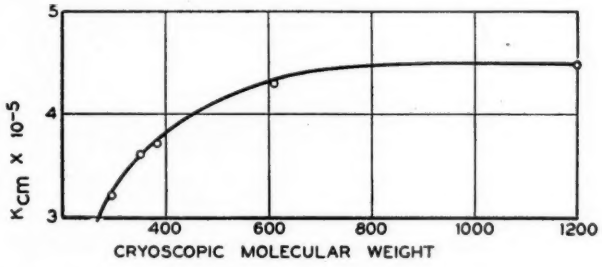

FIG. 2.—Relation between K_{cm} and molecular weight of polystyrene.

the chain. DeBoer[3] presented evidence to show that the benzene rings in the polystyrene molecule take a perpendicular position with respect to the chain. The molecular weight dependency of K_{cm}, shown in Figure 2, may be explained by the greater mobility of the lower polymers together with the increased influence of the end bonds with decreased chain length, thus increasing viscosity and reducing K_{cm}. If we assume that the chain in a styrene trimer is made effectively longer by end bonds equal in effective length to the distance between two chain atoms, then K_{cm} of the trimer would be $6/7 \times 0.45 \times 10^4$ or 0.35×10^4, which agrees with the experimental results.

From the results of Staudinger and his coworkers[4], K_{cm} values were calculated for polyindene and hydrogenated polyindene up to molecular weights of 1600, and found to lie between 0.58×10^4 and 0.70×10^4. In the case of fractions with molecular weights between 2800 and 6000, the values rose from 1.2×10^4 to 1.6×10^4, respectively; probably this result was due to the failure of the higher polymer solutions to obey Raoult's law, thereby giving cryoscopic molecular weights which were too high.

The K_{cm} value selected for use for styrene polymers higher than the octamer is 0.45×10^4. In the case of the polyindene, a K_{cm} value of 0.6×10^4 was selected as the result of analysis of the present data. Polyindene is believed to polymerize, at least in part, in large rings; therefore, one would expect its K_{cm} value to exceed that for polystyrene. The difference, however, is small, and may be due to structural differences in the two hydrocarbons.

If the molecular weight of the highest polymeric fraction of styrene described by Staudinger[2] is calculated using Equation 2 and a K_{cm} value of 0.45×10^4, the result is 180,000 instead of 660,000, calculated by the use of the Staudinger Equation 1 and a K_m value of 1.8×10^{-4}.

The value of molecular weight obtained from viscosity data is based on the assumption that only linear polymers are involved, whereas branch chaining and cross-linking may result from certain polymerization reactions. Since viscosity measures the over-all polymer length rather than molecular weight, a K_{cm} value established for linear polymers will yield molecular weights which are too low when applied to cross-linked or branched-chain polymers of the same base molecule.

SOLVENT EFFECTS

The results in Table IV show that polystyrene up to 98,000 molecular weight is remarkably free from solvent effects and that numerous solvents can

TABLE IV

VISCOSITY OF POLYSTYRENE FRACTIONS IN DIFFERENT SOLVENTS AS COMPARED WITH BENZENE

Fraction	Mol. wt.	Solvent	Concn. (base molal)	η_r	Log η_r / C	$\left(\frac{\text{Log } \eta_r}{C}\text{ solvent} \Big/ \frac{\text{Log } \eta_r}{C}\text{ benzene}\right) \times 100$
Unfractionated low polymer	500	Benzene	0.800	1.238	0.116	100
		Chloroform	0.800	1.245	0.119	103
		CCl_4	0.800	1.307	0.145	125
A_4 polymer	600	Benzene	0.640	1.240	0.146	100
		Cyclohexane	0.558	1.211	0.149	102
B_4 polymer	2,400	Benzene	0.317	1.475	0.531	100
		Cyclohexane	0.273	1.307	0.426	81
Commercial polystyrene	18,600	Benzene	0.0500	1.606	4.13	100
		Chloroform	0.0504	1.600	4.05	98
		CCl_4	0.0504	1.561	3.84	93
Commercial polystyrene	53,500	Benzene	0.015	1.509	11.9	100
		Chloroform	0.015	1.480	11.3	95
		CCl_4	0.015	1.419	10.1	85
Polystyrene fraction	93,100	Benzene	0.010	1.612	20.7	100
		Chloroform	0.010	1.560	19.3	93
		CCl_4	0.010	1.492	17.4	84
		Tetralin	0.010	1.577	19.7	95
Polystyrene fraction	98,100	Benzene	0.010	1.651	21.8	100
		Chloroform	0.010	1.613	20.7	95
		CCl_4	0.010	1.531	18.5	85
		Tetralin	0.010	1.600	20.4	94

be used to determine its viscosity–molecular weight. Cyclohexane is a poor solvent, probably accounting for the decrease in viscosity as molecular weight increases. Carbon tetrachloride shows this same effect to a lesser degree, but forms solutions of low-polymer styrene having high relative viscosity when compared with benzene.

Staudinger and Heuer[9] studied numerous solvents to determine the relative viscosities of two polystyrenes having molecular weights of 17,500 and 43,300, using K_{cm} of 0.45×10^4. The ratio of the $\log \eta_r/C$ values to that for the benzene solution taken as 100, ranged from 90 to 105; as a whole, this indicated a remarkable freedom from solvent effects of any magnitude.

The authors selected benzene as the most suitable solvent based on the data in Table IV, especially those data on high-molecular styrene fractions prepared by precipitation from commercial polystyrene having an average molecular weight of 54,000.

FRACTIONATION OF HIGH-MOLECULAR POLYSTYRENE

High-molecular polystyrene dissolved in benzene is not precipitated by the addition of acetone until a large proportion is added. Methyl alcohol, however, is a much stronger precipitating agent. In view of this fact, a mixture of equal volumes of acetone and alcohol was first employed to precipitate all but the lowest molecular portion. The higher fractions were thrown out of solution by adding acetone in a quantity only sufficient for partial precipitation. Data regarding this fractionation are given in Table V.

TABLE V

FRACTIONATION OF HIGH POLYMERIC STYRENE BY PARTIAL PRECIPITATION

Polymer	Percentage of original material	$\frac{\text{Log } \eta_r}{C}$ in benzene	Average mol. wt.[a]
Original	100	12.0	54,000
Unpptd. material[b]	5	2.65	12,000
Fraction I	57	14.1	63,500
Fraction I*A*[c]	15	20.7	93,000
Fraction IA_1[c]	11	21.8	98,000

[a] $M = (\log \eta_r \times 0.45 \times 10^4)/C$.
[b] Fraction obtained by adding excess precipitating agent following first partial precipitation of fraction I; precipitate discarded and solvent evaporated to obtain unprecipitated portion.
[c] I*A* obtained by partial precipitation of fraction I; IA_1 obtained from I*A* in same manner.

STAUDINGER'S VISCOSITY–MOLECULAR WEIGHT RULE

Staudinger[2] presented data on several polymeric hydrocarbons showing that, when their K_m constants were divided by the number of chain atoms in their base molecules, a so-called K_m equivalent constant varying from 0.75×10^{-4} to 0.90×10^{-4} was obtained. From these results he formulated a rule which stated, in effect, that the specific viscosity of equal base molecular concentrations of different hydrocarbons of the same molecular weight is proportional to the chain length of the molecule.

Using our data, which are relatively free from cryoscopic deviations, concentration effects and solvent influences, the K_m equivalent values in Table VI were computed, and are compared with those based on Staudinger's data.

It is seen, therefore, that our data do not support this Staudinger rule, and that if a fundamental basis for the viscosity–molecular weight relation exists, it must be stated in some different way. Staudinger and Leupold[10]

TABLE VI

CALCULATED K_m EQUIVALENT ON VARIOUS POLYMERIC HYDROCARBONS

	$K_m \times 10^4$		$K_{eq.} \times 10^4$	
	Staudinger	Authors[a]	Staudinger	Authors[a]
Paraffin	0.8	1.0[b]	0.80	1.0
Polyprene	3.0	3.2	0.75	0.8
Polyisobutylene	1.7	2.6	0.85	1.3
Polystyrene	1.8	5.6[c]	0.90	2.8
Polyindene	1.8	4.0	0.90	2.0

[a] Benzene used as solvent.
[b] Data for $C_{28}H_{58}$.
[c] $K_m = 6.4 \times 10^{-4}$ when molecular weight of polymer was 350.

state that "chain-equivalent solutions of different hydrocarbons with fiber molecules of the same molecular weight in the same solvent have the same specific viscosity".

If we compare chain-equivalent solutions of normal paraffin and polystyrene in benzene, each having a molecular weight of 14,000, the specific viscosities in the two cases are calculated to be 2.83 and 34.9, respectively, using a K_{cm} of 2.4×10^4 determined for octacosane and 0.45×10^4 for polystyrene. The chain-equivalent concentrations are 14 and 52 grams per liter, respectively. It is obvious from these results that this rule does not apply or even approach compliance.

RELATION BETWEEN K_{cm} CONSTANTS OF LINEAR POLYMERS

Since K_{cm} is calculated from the base molal concentration, the proportional weight of chain atoms to total base molecular weight of different polymers must be considered if some equivalent factor common to all linear hydrocarbon polymers is to be calculated. For example, paraffin has a base molecular weight of 14; therefore, each base molecule places 12/14 or 0.86 of its weight of carbon in its chain, whereas styrene has a base molecular weight of 104, and one base molecule places only 24/104 or 0.23 of its weight of carbon in the chain. On this basis alone the Staudinger K_m equivalent for polystyrene would be $(1.0 \times 0.86)/0.23 = 3.7 \times 10^{-4}$, compared with the authors' value of 3.2×10^{-4} for polystyrene given in Table VI.

If the K_{cm} equivalent to one carbon atom in the chain is calculated for various linear polymers, the following are some of the factors which need to be considered as influencing the results:

1. Molecular size distribution
2. Molecular weight level
3. Viscosity level
4. Concentration effects
5. Solvent effects
6. Number of chain atoms in the base molecules
7. Weight percentage of chain atoms to total base molecular weight
8. K_{cm} value of polymer in question
9. Distance between chain atoms
10. Structure of the base molecule (side-group effects)

Table VII was prepared to evaluate some of these factors from our own data and certain data selected from Staudinger's work which appears to be most reliable. The effect of distance between chain atoms in the different polymers is in most cases relatively small and was, therefore, not considered.

TABLE VII

CALCULATED K_{cm} EQUIVALENT OF VARIOUS LINEAR POLYMERS

Polymer	Formula	Mol. wt.	Solvent	A No. chain atoms in base mol.	$\frac{B}{K_{cm}}$	C Wt. proportion, chain atoms in base mol.	K_{cm} equivalent, $(A \times B)/C$
Tetradecane to Octa-cosane[a]	$C_{14}H_{30}$ to $C_{28}H_{58}$	198 to 394	Benzene	1	4.05×10^4 to 2.38×10	0.85	4.7×10^4 to 2.8×10^4
Same[a]	Same	Same	*n*-Hexane	1	1.83×10^4		2.2×10^4
Paraffins with side groups[b]	$C_{20}H_{42}$ to $C_{46}H_{94}$	282 to 647	Benzene	1	2.44×10^4 to 2.64×10^4	0.68 to 0.81	3.1×10^4 to 3.6×10^4
Squalene[b]	$H(C_5H_8)_6H$	410	Benzene	4	0.66×10^4	0.70	3.8×10^4
Polyprene	$(C_5H_8)_n$	1200	Benzene	4	0.75×10^4	0.71	4.2×10^4
Polyisobutylene	$(C_4H_8)_n$	1080	Benzene	2	0.95×10^4	0.43	4.4×10^4
		358	*n*-Hexane	2	0.66×10^4	0.43	3.1×10^4
		456	*n*-Hexane		0.71×10^4	0.43	3.3×10^4
		1080	*n*-Hexane		0.75×10^4	0.43	3.5×10^4
Polystyrene	$(C_8H_8)_n$	350	Benzene	2	0.36×10^4	0.23	3.1×10^4
		600	Benzene		0.43×10^4	0.23	3.7×10^4
		1180	Benzene		0.45×10^4	0.23	3.9×10^4
Polyethylene oxide dihydrate[b]	$H(C_2H_4O)_nH$	800 to 1200	Benzene	3	1.1×10^4	0.91	3.6×10^4
Cellulose acetate[b]	$[C_6H_7O_5(CH_3CO)_3]_n$	1150 to 2890	Dioxane	5	0.21×10^4	0.22	4.8×10^4
Cellulose nitrate[b]	$[C_6H_7O_5(NO_2)_3]_n$	1485 to 106,000	Butyl acetate	5	0.19×10^4	0.21	4.5×10^4

[a] Data to be published. [b] Staudinger's data.

With the exception of the paraffins, the calculated K_{cm} equivalent lies between 3.1 and 4.8. This is rather remarkable, in view of the numerous variables which may influence the results. The average K_{cm} equivalent per chain atom, not including the lower polyisobutylene or polystyrene polymers, is about 4×10^4.

In our series of measurements of normal paraffin hydrocarbons in benzene ranging from $C_{16}H_{34}$ to $C_{28}H_{58}$ given in Table VII, the K_{cm} equivalent values decrease from 4.0 to 2.8, respectively, whereas the hexane solutions give a constant K_{cm} value as the chain length increases.

Judging from the K_{cm} equivalent values in Table VII for the paraffins and polyisobutylenes in *n*-hexane, it is indicated that polymers with side groups which increase the width of the molecule give higher K_{cm} equivalents. The decrease in the K_{cm} values for the normal paraffins in benzene as chain length increases was also in evidence in the case of polyisobutylene in the same molecular weight range. This is a special solvent effect, and is discussed in connection with polyisobutylene[7].

Staudinger's K_{cm} values for polyprene, polyisobutylene, and polystyrene give K_{cm} equivalent values of 5.2×10^4, 6.5×10^4, and 12.2×10^4, respectively. These high values are mainly due to the fact that the cryoscopic molecular weight data employed by Staudinger were obtained on polymer solutions which deviated widely from Raoult's law.

The agreement in the K_{cm} equivalents lends considerable weight to the view that the viscosity method for determining the molecular weight of linear polymers is quite reliable when suitable solvents are selected and a reliable K_{cm} value is employed. There still remains, however, a lack of certainty that in some cases a true molecular dispersion of the polymer exists in solution. In the case of polystyrene, however, the fact that the same viscosity is obtained with different solvents is evidence that complete molecular dispersion probably is obtained.

The question as to the reliability of the osmotic method compared to the viscosity method for molecular weight determination cannot be finally settled

at this time. This is because the viscosity method is well established for the lower polymeric range, but its application must be assumed in the higher range of molecular weights where reliable independent methods are not available. Due to experimental complications, the osmotic method cannot readily be employed in the case of the lower polymers, and since the higher polymer solutions deviate widely from Raoult's law, the results by the osmotic method are believed to be inordinately high. Outside the range of ideal solutions the molecular weight values obtained by the cryoscopic method are also too high, as shown in previous work[5] by the increase in the K_{cm} value as the molecular weight increases.

SUMMARY

1. The cryoscopic method is not satisfactory for polystyrenes containing more than twelve styrene units in the chain on account of the failure of their solutions to obey Raoult's law.

2. The present work has established a new K_{cm} value of 0.45×10^4 for benzene solutions of polystyrene to be used in the equation:

$$M = \frac{\log \eta_r}{C} \times K_{cm}$$

A K_{cm} value of 0.6×10^4 has been similarly established for benzene solutions of polyindene.

3. Increased confidence in the viscosity–molecular weight procedure is derived from the data presented for the new K_{cm} equivalent covering a wide range of different polymers.

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CRYOSCOPIC AND VISCOSITY STUDIES OF POLYISOBUTYLENE

CRYOSCOPIC DEVIATION OF POLYISOBUTYLENE SOLUTIONS FROM RAOULT'S LAW *

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The high degree of chemical stability and excellent dielectric properties of polyisobutylene have led to its widespread commercial use. Polymers of isobutylene are available ranging from viscous liquids to rubberlike elastomers. Since these progressive changes result from various degrees of polymerization, the products are characterized in accordance with their average molecular weights. It is important, therefore, to have a satisfactory method for reliably determining the average molecular weight of different preparations. It is also desirable to provide methods of fractionation to determine the polymer size distribution as this also affects physical properties.

The Staudinger viscosity method has been used to determine the average molecular weight of polyisobutylene using an aliphatic hydrocarbon solvent such as *n*-hexane or *n*-heptane. This method, however, is subject to the effect of a wide range of variables which may profoundly affect the results. It is therefore necessary to make a detailed study of this method as applied to polyisobutylene before its reliability can be determined.

A previous paper[1] showed that the cryoscopic method deviates from Raoult's law in the case of polyprenes having degrees of polymerization in excess of about 20 isoprene units. Recognition of this fact led to a new K_{cm} constant for rubber of 0.75×10^4, which is 25 per cent lower than that employed by Staudinger. This and previous work by the authors[1] has also led to the adoption of the equation:

$$M = \frac{\log \eta_r \times K_{cm}}{C} \tag{1}$$

instead of the Staudinger equation:

$$M = \frac{\eta_{sp}}{C \times K_m} \tag{2}$$

for calculating the molecular weight from viscosity data.

Previous work relating to the viscosity and cryoscopic molecular weight of low-polymeric isobutylene was carried out by Staudinger and Brunner[2]. In this work, however, only one cryoscopic measurement in benzene was made by these authors on a low polymer yielding a value of 1496. The viscosity of a 0.5 base molal solution of this polymer in Tetralin was measured, giving a η_r value of 1.13. From these data the value of K_{cm} is calculated to be 1.4×10^4. A K_{cm} value of 1.3×10^4 was recently employed by Thomas, Zimmer, Turner, Rosen, and Frolich[3] in their study of polyisobutylene.

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In view of this lack of data on the viscosity–molecular weight relation of polyisobutylene solutions, it was thought desirable to conduct the present investigation. Cryoscopic and viscosity measurements were carried out on polymers differing widely in average molecular weight and distribution. Solvent effects were also investigated to specify proper procedures for the conduct of viscosity–molecular weight measurements. The influence of concentration and degree of polymerization on cryoscopic measurements was studied to determine the deviations of these solutions from Raoult's law.

MATERIALS

Polyisobutylene trimer was obtained from a crude trimer (kindly furnished by L. B. Turner of the Standard Oil Development Company of New Jersey) by distillation in a 12-inch, air-jacketed, multiple, concentric-tube column; the result was that 85 per cent distilled between 123° and 170° C, whereas 55 per cent distilled between 168° and 170° C. The fraction distilling at 170° C was selected for use. Its refractive index at 25° C was 1.4318. The boiling point and refractive index given in the literature for pure trimer are 176° to 178° C and 1.4306, respectively.

The heptamer and nonamer fractions were obtained by first cracking C polymer in vacuum at 360° C until 90 per cent distilled over. This distillate was then fractionated under vacuum in the concentric-tube column described above. The fractionation was carried out on 100 cc. of the cracked distillate at successively lower pressures starting at 23 and ending at 1.4 mm. The fractions obtained are shown in Table I. The cracking and distillation work was carried out by M. L. Selker of these laboratories.

TABLE I

FRACTIONATION OF CRACKED POLYISOBUTYLENE

Fraction no.	Approx. b. p. (° C)	Approx. pressure (mm.)	Volume (cc.)	Refractive index, n_D^{25}
1	136	23	8	1.4540
2	159	13	6	1.4640
3	165	6	16	1.4704
4	150	1.5	4	1.4733
5	130	1.4	21	1.4764
6	...	1.4	10	1.4801
Residue	...	...	33	1.4880
			Total 98	

Fractions 3 and 5 were selected for cryoscopic and viscosity studies since they consist largely of heptamer and nonamer, respectively. Iodine values of the lower fractions were determined by dissolving 0.25-gram samples in 10 cc. of chloroform and adding 25 cc. of 0.2 *N* Wijs solution. The flask containing the solution was immediately surrounded with cracked ice in darkness, and the titration of excess iodine determined after standing one hour. It was found that substitution occurred in light and at ordinary temperature. The results obtained under various conditions are given in Table II. A possible explanation for the lower iodine value found for the trimer fraction is that some cyclization took place during its preparation. The values for the heptamer and nonamer fractions agree closely with theory.

Starting material C was a commercial liquid isobutylene polymer (supplied by the Standard Oil Development Company of New Jersey). It had been

TABLE II

IODINE VALUE OF ISOBUTYLENE FRACTIONS

Substance	Reaction period (hrs.)	Temp. of reaction (°C)	Light conditions	Iodine value	
				Found	Theory
Trimer[a]	0.5	0	Dark	81.0	151.2
	1.0	0	Dark	91.4	
	3.0	0	Dark	91.2	
	3.0	25	Dark	95.0	
Heptamer (fraction 3)	1.0	0	Dark	65.1	64.8
	1.0	0	Light	69	
	1.0	25	Light	79	
	4.0	25	Light	85	
Nonamer (fraction 5)	1.0	0	Dark	50.3	50.8
	1.0	25	Light	67	
	4.0	25	Light	74	

[a] Trimer analyzed as follows:

	Carbon	Hydrogen	Ratio H/C
Found	85.20	14.03	1.96
Theory $(C_4H_8)_3$	85.62	14.38	2.00

made in such a manner as to yield a product having a narrow molecular weight distribution. By washing this material with a mixture of equal volumes of *n*-hexane and methanol, a total of 12 per cent was extracted after five separate treatments. The viscosity of the extracted polymer was determined in benzene and gave a value for log η_r/C of 0.095 against 0.125 for the original material and 0.135 for the residue, C_2, after extraction. Attempts to precipitate this polymer from hexane solution by adding methanol resulted in complete precipitation of the liquid polymer in a narrow range of alcohol addition, indicating the absence of higher polymeric fractions. The polymer size distribution of this fraction is extremely narrow, probably varying not in excess of ±10 per cent from the average molecular weight.

Material D obtained from the same source was much more viscous than C. Fractional precipitation by adding acetone to a solution of it in hexane yielded fractions ranging in average molecular weight from about 900 to 4000. About 65 per cent of this material consists of a polymer similar to material C and the remainder is a polymer having an average molecular weight of about 4000. Data on the fractionation of material D are given in Table III.

TABLE III

FRACTIONATION OF D POLYMER

Material	Percentage of original material	$\frac{\text{Log } \eta_r}{C}$ in C_6H_6
D (original)	100	0.222
D_2, unpptd. portion of D	37	0.086
D_3, first pptd. portion of D	63	0.294
D_4, unpptd. portion of D_3	24	0.094
D_5, pptd. portion of D_3	39	0.397
D_6, unpptd. portion of D_5	4	...
D_7, pptd. portion of D_5	35	0.427

Material E is a commercial polymer from the same source as C and D. This material has a very narrow polymeric range as judged from the fact that a 90 per cent fraction prepared by double precipitation as in the case of D

had a log η_r/C value in benzene of 0.680 as compared with 0.630 for the original E material.

With the exception of the three lower polymers, all fractions used for cryoscopic measurements were heated to constant weight under high vacuum at 100° C to remove residual solvent.

CRYOSCOPIC–VISCOSITY MEASUREMENTS

The cryoscopic measurements in C. P. benzene and C. P. cyclohexane[1] were made in a standard manner. Excess supercooling was avoided, and the solution was vigorously and uniformly stirred to establish temperature equilibrium in a short period. Three freezing point determinations were made on each solution, and variations not in excess of ±0.001° C were realized unless some disturbing factor occurred which is noted. Viscosity measurements were conducted at 25° C, as described in a previous publication[1].

The cryoscopic-viscosity data in different polyisobutylene preparations given in Table IV lead to the selection of the value for K_{cm} of 1.0×10^4 in

TABLE IV

VISCOSITY–MOLECULAR WEIGHT CONSTANTS OF POLYISOBUTYLENE FRACTIONS

Solvent	Concentration: Base molal	Concentration: g./100 g. solvent	η_r	$\frac{\text{Log } \eta_r}{C}$	$\Delta_1° - \Delta°$	Cryoscopic mol. wt.	$K_{cm} \times 10^{-4}$
			Trimer				
C_6H_6	0.355	3.28	...	...	0.705	168	1.49
	2.84	...	1.059	0.088	...	...	...
	4.68	...	1.130	0.113	...	...	...
			Heptamer				
C_6H_6	...	2.62	...	...	0.380	353	0.89
	...	5.40	...	...	0.763	362	0.91
	1.596	11.38	1.143	0.364	1.499	389	...
	2.90	...	1.305	0.398	...	...	...
			Nonamer				
C_6H_6	...	2.62	...	...	0.295	455	0.92
	...	5.40	...	...	0.602	460	0.93
	1.596	11.42	1.176	0.440	1.178	495	...
	2.90	...	1.389	0.493	...	...	...
			Polymer C				
C_6H_6	0.389	2.54	1.122	0.128	0.128	950	0.74
	0.779	5.20	1.252	0.125	0.260	1030	0.83
	1.559	11.00	1.569	0.125	0.509	1110	0.89
			Fraction C_1 (C washed with alcohol-hexane mixture)				
C_6H_6	0.429	2.80	1.136	0.129	0.134	1070	0.83
	0.857	5.77	1.288	0.128	0.258	1150	0.90
			Fraction C_2 (C_1 washed with alcohol-hexane mixture)				
C_6H_6	0.204	1.31	1.053	0.110	0.065	1030	0.94
	0.408	2.65	1.119	0.120	0.121	1130	0.95
	0.815	5.44	1.266	0.126	0.235	1190	0.95
	1.630	11.50	1.689	0.135	0.468	1260	0.94
C_6H_{12}	0.201	1.48	1.098	0.202	0.292	1020	0.70[a]
	0.402	2.96	1.193	0.190	0.623	970	0.67
	0.804	6.12	1.408	0.185	1.262	980	0.67
	1.607	12.92	1.985	0.185	1.957	1330	0.92

TABLE IV—*Continued*

Solvent	Concentration: Base molal	Concentration: g./100 g. solvent	η_r	$\frac{\text{Log } \eta_r}{C}$	$\Delta_1° - \Delta°$	Cryoscopic mol. wt.	$K_{cm} \times 10^{-4}$
			Polymer D				
C_6H_6	0.445	2.90	1.256	0.222	0.113	1320	0.60
	0.890	5.98	1.572	0.221	0.231	1320	0.60
	1.779	12.75	2.544	0.228	0.460	1410	0.62
			Fraction D_1 (fraction D washed with alcohol-hexane mixture)				
C_6H_6	0.830	5.56	1.547	0.228	0.198	1430	0.63
	1.660	11.78	2.393	0.228	0.411	1460	0.64
			D_2 (low-molecular portion from D)				
C_6H_6	0.855	5.74	1.184	0.086	0.330	890	1.03
			D_7 (high-molecular portion from D)				
C_6H_6	0.535	...	1.695	0.427	Uncertain	...	...
	0.892	5.94	2.410	0.427	Uncertain	...	...
C_6H_{12}	0.144	1.05	1.286	0.760	0.027	7800	1.43[a]
	0.287	2.11	1.606	0.715	0.063	6800	1.24
	0.575	4.32	...	...	0.159	5500	1.01
	1.150	8.80	...	...	0.437	4090	0.73
			High-molecular portion D_7 broken down by heating (unfractionated)				
C_6H_6	0.127	0.82	1.123	0.398	0.018	2330	0.58
	0.253	1.64	1.263	0.400	0.036	2320	0.58
	0.506	3.34	1.608	0.407	0.078	2200	0.53
	1.012	6.82	2.666	0.420	0.154	2270	0.55
			Polymer E				
C_6H_6	0.149	0.96	1.263	0.680	0.007	(7050)[b]	1.04
	0.149	0.96	1.263	0.680	0.008	(6160)	0.91
	0.298	1.94	1.518	0.640	0.017	(5850)	0.92
	0.298	1.94	1.518	0.640	0.022	(4520)	0.71
	0.595	3.95	2.511	0.670	0.027	(7500)	1.12
	0.595	3.95	2.511	0.670	0.037	(5450)	0.82
	1.190	8.23	...	...	Very uncertain, difficult to crystallize		...
C_6H_{12}	0.134	0.975	1.493	1.30	0.023	8500	1.00[a]
	0.268	1.95	2.114	1.21	0.059	6700	0.80
	0.536	3.97	3.857	1.10	0.138	5800	0.70
	1.072	8.26	...	...	0.363	4600	0.55

[a] Using average log η_r/C of *n*-hexane solutions in Table VI.
[b] Values in parentheses were obtained by a different procedure, which makes them less reliable than the others.

benzene or about 40 per cent less the value based on the limited data of Staudinger and Brunner[2]. Benzene, however, is a poor solvent for polyisobutylene and therefore cannot be employed, as will be shown later. For this reason, good solvents such as *n*-hexane or chloroform must be used, and the K_{cm} value based on these solvents.

The present data, especially that on polymer D, illustrate the effect of polymer size distribution on cryoscopic measurements. This material is essentially a mixture containing 65 per cent of a narrow polymer fraction having an average molecular weight of about 1000 and 35 per cent of a polymer with an average molecular weight of about 4000. The weight average molecular weight of this mixture is 2050. The calculated cryoscopic molecular weight of this mixture is 1360, which is in close agreement with the value of 1350 actually determined. It is readily seen, therefore, why the K_{cm} value of 0.60 is too

low, since it is based on a low cryoscopic value caused by the distribution effect. For this reason the utmost care must always be taken to base K_{cm} values only on narrow polymer fractions which are completely free from residual solvents.

DEVIATION OF SOLUTIONS FROM RAOULT'S LAW

Data given in Table IV and Figure 1 on polymers ranging in molecular weights from 400 to 1400 show little cryoscopic deviation with increased concentration. Some concentration effect is evidenced in the case of the lower

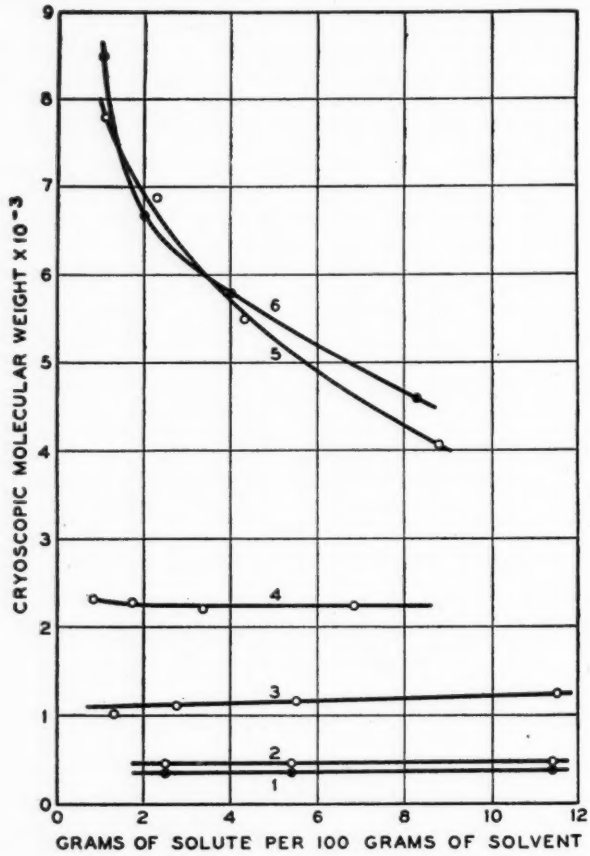

FIG. 1.—Effect of concentration on cryoscopic measurements of polyisobutylene solutions.

1. Heptamer in benzene
2. Nonamer in benzene
3. Fraction C_2 in benzene
4. Fraction D_4 in benzene
5. Fraction D_7 in cyclohexane
6. Polymer E in cyclohexane

polymers, which is believed to be the result of molecular association at the higher concentrations. Cryoscopic values of very low molecular weight polymers in the concentration range of 1 to 3 per cent are therefore considered most reliable. In the case of polymers with average molecular weights of 4000 to 6000, large negative deviations of molecular weight with increased

concentration were found, as in the case of polyprenes in the previous study[1]. Negative deviations occur when the molecular weight exceeds about 2300, corresponding to a degree of polymerization of about 40 isobutylene units or 80 carbon atoms in the chain. Both polyprene and polyisobutylene therefore begin to show negative deviation from Raoult's law when the same number of carbon atoms are in the chain. The positive association effect would, if it were considered, lower this estimate somewhat.

The concentration effect will depend somewhat on the distribution. Polymer E has a wider distribution than preparation D_7, which can account for the greater concentration effect of D_7 than E in spite of the fact that D_7 has the lower viscosity–molecular weight value.

Cryoscopic measurements of benzene solutions of D_7 and E polymers were unsatisfactory. When crystallization was started following supercooling, large temperature rises were noted on stirring which in some cases were as much as 2° C above the freezing point of pure benzene. This did not occur in the case of the cyclohexane solutions. The values obtained for polymer E in benzene were obtained by causing heavy crystallization to occur, allowing most of the crystals to melt gradually, and then taking the highest equilibrium temperature. The results show that this method is not satisfactory. The large temperature rise on crystallization is an unusual effect, which we have also noted in a similar case with benzene solutions of polystyrene. It is possible that a benzene polymer complex is formed which crystallizes on cooling and gives up a large amount of heat. This effect was not noted in the previous investigation[1] of benzene solutions of polyprene in the same molecular weight range.

Meyer[4] advanced an explanation for the failure of the higher polymers to obey Raoult's law in osmotic measurements, based on the idea of segment action of polymer chains. This segment theory was further developed by Powell, Clark, and Eyring[5] and Powell and Eyring[6] who calculated various segment lengths for different polymers.

The effect of concentration on cryoscopic measurements of nonideal polymer solutions may depend on decreased thermal motion of the polymer as its chain length increases, which results in decreased interchange of position of polymer and solvent molecules.

When the molecular weights of high polymers are calculated from osmotic pressure data, the practice is to extrapolate P/c values to the zero concentration ordinate and use this value to calculate molecular weight by the formula:

$$M = \frac{RT}{P/c}$$

This method, which is applicable to ideal solutions in accordance with van't Hoff's law, leads to inordinately high values when applied to nonideal polymer solutions, compared with those obtained by the viscosity method.

If freezing point lowering over concentration is plotted against concentration, the extrapolation of Δ/C to the zero concentration ordinate and the use of this value in the equation:

$$M = \frac{f \times 10}{\Delta/C}$$

also leads to inordinately high molecular weight values and high values for K_{cm}. This is seen in the case of the polyprene and polyisobutylene fractions

of Figure 2; as the viscosity–molecular weight increases, the cryoscopic molecular weight obtained by extrapolation of Δ/C to the zero concentration ordinate becomes greater. An almost identical type of plot of P/c against concentration is shown by Mark[7] for various polymers. The same conclusion can be

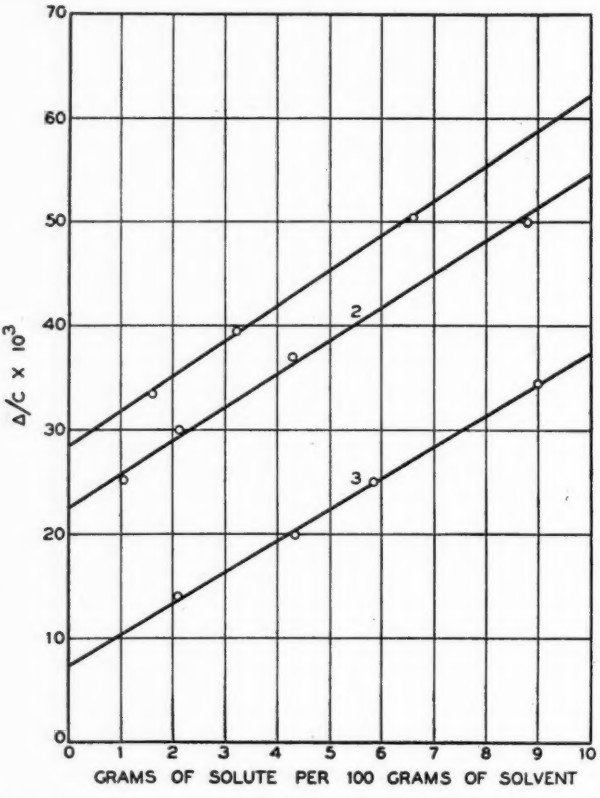

FIG. 2.—Relation between freezing point lowering and concentration of polymers in cyclohexane.

Polymer	Viscosity–mol. wt.	$M = \frac{f \times 10}{\frac{\Delta}{C} \to 0}$
1. Polyprene	4100	8,000
2. Polyisobutylene E	6300	9,000
3. Polyprene	7300	27,000

TABLE V

COMPARISON OF OSMOTIC AND VISCOSITY MOLECULAR WEIGHTS

Substance	Osmotic mol. wt.	Viscosity mol. wt.	Ratio
Methyl ester of polyoxyundecanoic acid in benzene[8]	3,100	2,100	1.5
	23,600	11,800	2.0
	35,000	13,500	2.6
Gutta-percha hydrocarbon in toluene[9]	105,000	43,800	2.4
Milled crepe rubber in toluene[9]	270,000	60,000	4.5
Crepe rubber in benzene	500,000[9]	105,000[11]	4.8

TABLE VI

VISCOSITY OF POLYISOBUTYLENE FRACTIONS IN DIFFERENT SOLVENTS AS COMPARED WITH *n*-HEXANE[12] AT 25° C

Fraction	Solvent	Concn. (base molal)	η_r	$\frac{\text{Log } \eta_r}{C}$ Value	$\frac{\text{Log } \eta_r}{C}$ Ratio to *n*-hexane as 100
Trimer	*n*-Hexane[a]	2.840	1.187	0.0262	100
		4.680	1.352	0.0279	...
	Benzene	2.840	1.059	0.0088	34
		4.680	1.130	0.0113	43
Heptamer	*n*-Hexane[a]	2.900	1.434	0.0540	100
	Benzene	1.596	1.143	0.0364	67
		2.900	1.305	0.0398	74
Nonamer	*n*-Hexane[a]	2.900	1.534	0.0640	100
	Benzene	2.900	1.389	0.0493	77
C_2 polymer (1080 mol. wt.)	*n*-Hexane[a]	0.800	1.306	0.145	100
	Benzene	0.815	1.266	0.126	87
	Chloroform	0.800	1.300	0.142	98
	Cyclohexane	0.804	1.408	0.185	128
	Tetralin	1.032	1.415	0.146	100
Low polymer (1700 mol. wt.)	*n*-Hexane[a]	1.745	1.700	0.226	100
	Benzene	1.625	1.525	0.193	85
	Chloroform	1.625	1.643	0.227	100
	CCl_4	1.666	1.818	0.267	118
Low polymer (4100 mol. wt.)	*n*-Hexane[a]	0.651	2.027	0.547	100
	Benzene	0.535	1.695	0.427	78
	Chloroform	0.528	1.943	0.545	100
	Cyclohexane	0.287	1.606	0.715	131
E polymer (6300 mol. wt.)	*n*-Hexane[a]	0.300	1.791	0.840	100
	n-Hexane[b]	0.357	1.877	0.766	91
	Benzene	0.300	1.533	0.620	74
	Chloroform	0.300	1.795	0.840	100
	Cyclohexane	0.300	2.176	1.130	135
Commercial high polymer (30,000 mol. wt.)	*n*-Hexane[a]	0.100	2.483	3.95	100
	Benzene	0.100	1.637	2.14	54
	Chloroform	0.100	2.420	3.84	97
	CCl_4	0.100	2.975	4.74	120
	Cyclohexane	0.100	3.370	5.23	132
Commercial high polymer (50,000 mol. wt.)	*n*-Hexane[a]	0.050	2.151	6.65	100
	n-Hexane C. P.[b]	0.0357	1.636	6.00	90
	Benzene	0.050	1.443	3.20	48
	Chloroform	0.050	2.150	6.65	100
	Neohexane C. P.	0.050	1.815	5.18	78
	n-Heptane C. P.	0.050	2.074	6.33	95
	CCl_4	0.050	2.513	8.00	120
	Cyclohexane C. P.	0.050	2.959	9.42	142
Commercial high polymer (100,000 mol. wt.)	*n*-Hexane[a]	0.025	2.191	13.6	100
	Benzene	0.025	Only partially sol.		
	Chloroform	0.025	2.150	13.3	98
	Cyclohexane	0.025	3.098	19.6	144

[a] Skellysolve B ($n_D^{20} = 1.3844$, $d_4^{20} = 0.6822$).
[b] Eastman's C. P. grade ($n_D^{20} = 1.3759$, $d_4^{20} = 0.6617$).

made with respect to recent data published by Staudinger and Nuss[8] and by Staudinger and Fischer[9]. A comparison of osmotic molecular weights with those obtained by viscosity are given in Table V. These results explain the decrease in K_m values with increasing molecular weights as recently discussed by Meyer[10]. In this work Meyer showed that the Staudinger K_m constant decreased with increasing molecular weight of numerous polymeric substances covering a wide range of polymeric size. Similar increases in K_{cm} would, of course, be shown by these results. The results cited by Meyer are for the most part based on molecular weight of higher polymers, determined cryoscopically and osmotically. The present evidence indicates that both the cryoscopic and osmotic methods give results which deviate from the true value to an increasing extent as the molecular weight increases.

Although extrapolation of osmotic pressure or cryoscopic data from ideal solutions of high polymers to infinite dilution is thermodynamically sound, the same treatment of similar data from nonideal polymer solutions is open to question. Since K_{cm} in Equation 1, calculated from such extrapolated values, increases sharply with polymer size in nonideal solutions, these changing K_{cm} values must be viewed as simply reflecting the increasing deviations from Raoult's law.

In view of this situation, the authors have chosen to accept the reliability of Equation 1 when suitable solvents and conditions are selected, and the K_{cm} value has been established from the viscosity of the highest polymer fraction whose solution obeys Raoult's law.

SOLVENT EFFECTS

Since benzene is not a good solvent for high-molecular polyisobutylene, it is necessary to compare the viscosity of various polymer fractions in other solvents to determine the correct K_{cm} value to use with a good solvent. The

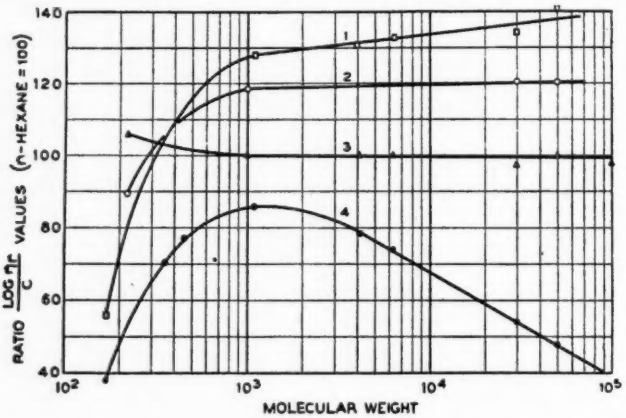

FIG. 3.—Comparative viscosity-concentration relation of polyisobutylene fractions in various solvents.
1. Cyclohexane solutions
2. Carbon tetrachloride solutions
3. Chloroform solutions
4. Benzene solutions

data in Table VI and Figure 3 illustrate clearly the care that must be taken in the selection of solvents for use in viscosity–molecular weight studies.

In the case of a poor solvent such as benzene, as the molecular weight of the polymer increases, the relative values of log η_r/C increase to a maximum,

then decrease in comparison with the better solvents such as hexane or chloroform. On the other hand, the ratio of log η_r/C between hexane solutions and those using other good solvents remains practically constant throughout the whole polymeric range.

Although chloroform containing 0.7 per cent alcohol as a stabilizer is a satisfactory solvent, *n*-hexane (Skellysolve) is preferred for general use. Whereas C. P. *n*-hexane or *n*-heptane might be considered best for research studies, they are much more costly. Furthermore, our experience with Skellysolve has shown that this product is remarkably uniform.

MOLECULAR WEIGHT DEPENDENCY OF K_{cm} CONSTANT

It was shown[1] in the case of polyprene that, whereas Staudinger found squalene and hydrosqualene to give K_{cm} values in benzene of 0.65×10^4 and 0.67×10^4, respectively, the authors obtained a value of 0.75×10^4 for low-polymeric fractions of rubber. In Table VII the K_{cm} values of the low isobutylene polymer in *n*-hexane are compared with the value obtained with a narrow fraction having a molecular weight of 1080. These data are plotted in Figure 4 and show the molecular weight dependency of K_{cm} in the case of isobutylene polymers having molecular weights less than about 1000. (Similar results have been obtained in the case of low styerne polymers.)

TABLE VII

VISCOSITY–MOLECULAR WEIGHT CONSTANTS OF POLYISOBUTYLENE FRACTIONS IN *x*-HEXANE

Fraction	Cryoscopic mol. wt.	$\frac{\text{Log } \eta_r}{C}$	$K_{cm} \times 10^{-4}$
Trimer	168	0.028	0.60
Fraction 3 (heptamer)	358	0.054	0.67
Fraction 5 (nonamer)	456	0.064	0.71
C_2	1080	0.145	0.75

The explanation for the relatively small increase in K_{cm} in the lower polymers, as shown in Figure 4, may lie in the proportionally larger effect of terminal

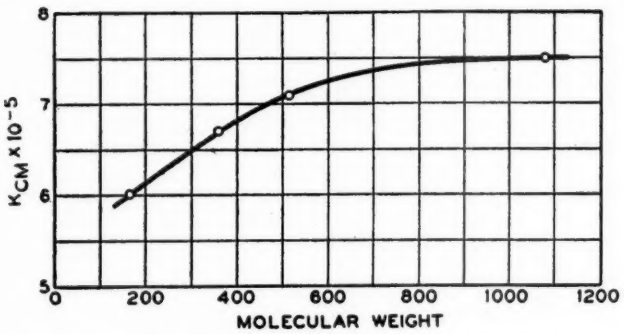

FIG. 4.—Effect of polymer size on K_{cm} value of polyisobutylene in *n*-hexane.

bonds. Another explanation may be based on the greater mobility or Brownian movement of the smaller polymeric molecules in solution, which would bring the side groups into play and thus increase the resistance to shear. When the molecules attain sufficient length, some degree of structural align-

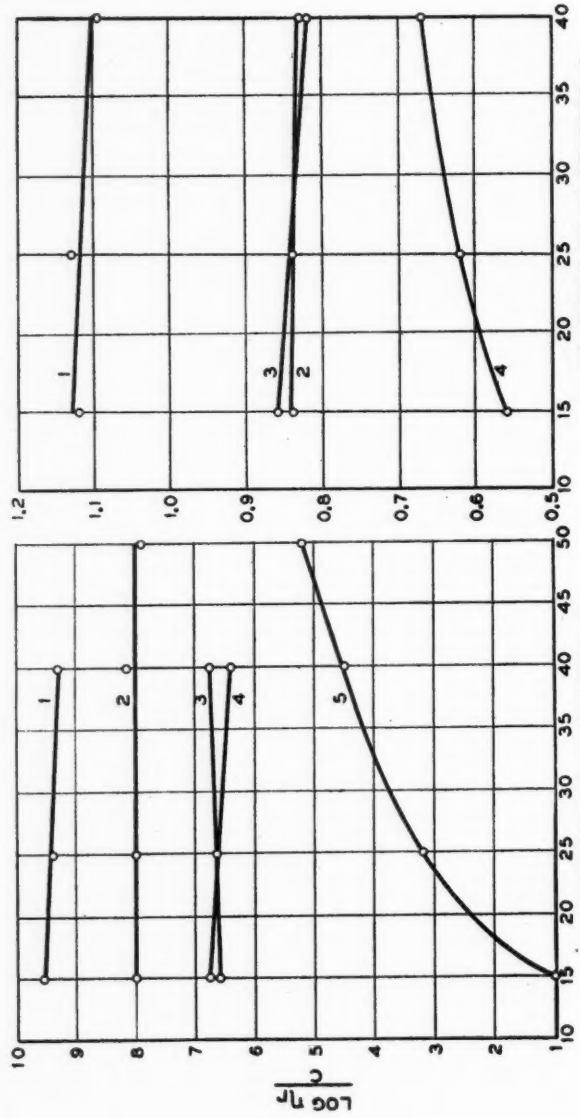

FIG. 5.—Effect of temperature on the relative viscosity of polyisobutylene in various solvents.

Polyisobutylene (50,000 mol. wt.)
1. Cyclohexane
2. Carbon tetrachloride
3. Chloroform
4. *n*-Hexane
5. Benzene

Polyisobutylene (6300 mol. wt.)
1. Cyclohexane
2. Chloroform
3. *n*-Hexane
4. Benzene

ment probably takes place during flow, and the viscosity becomes a true measure of the average polymer chain length at a fixed concentration, provided a condition of uniform and complete molecular dispersion exists.

The K_{cm} constant of 0.75×10^4 for polybutylenes dissolved in *n*-hexane (Skellysolve B) is considered to be a suitable selection, provided the molecular weight is 1000 or greater. It is 46 per cent lower than the value of 1.4×10^4 based on Staudinger and Brunner's limited study[2]. Referring to the data in Table VI, K_{cm} values of 0.82×10^4 and 0.79×10^4 are indicated for C. P *n*-hexane and *n*-heptane, respectively.

EFFECT OF TEMPERATURE ON VISCOSITY OF POLYISOBUTYLENE SOLUTIONS

The relatively poor solvent power of benzene for polyisobutylene polymers is illustrated in Figure 5 in comparison with other solvents. Benzene solutions of polyisobutylene show increasing temperature effects as the molecular weight increases. These results are to be expected if one considers that the polyisobutylene molecules are incompletely dispersed in the benzene, and therefore contribute less to the viscosity effect than would be the case if each of the

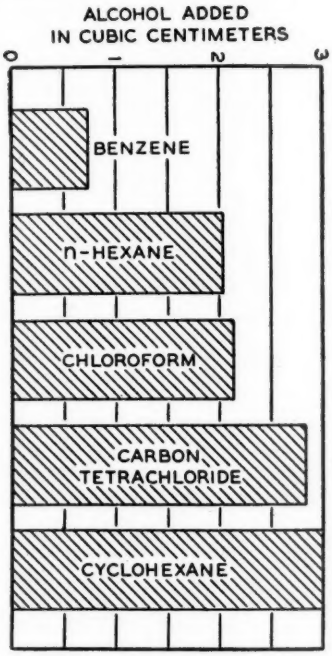

FIG. 6.—Amount of alcohol required to start precipitation of polyisobutylene (50,000 molecular weight).

polymer molecules were disentangled from one another. The temperature effect was found to be perfectly reversible, indicating some associated structural effect which changes in a definite way with temperature.

The data in Figures 6 and 7 also illustrate poor solvation by benzene, since a much smaller amount of alcohol is required for precipitation to start than is the case with better solvents, as judged by the first appearance of permanent

cloudiness of the solution. Figure 6 shows that the order is the same as the ratio of viscosities of polybutylene polymers in these solvents. The results in Figure 7 indicate that at higher temperatures the dispersive power of the benzene is higher and therefore more alcohol is required to cause precipitation. This agrees with the recent work of Evans and Young[12].

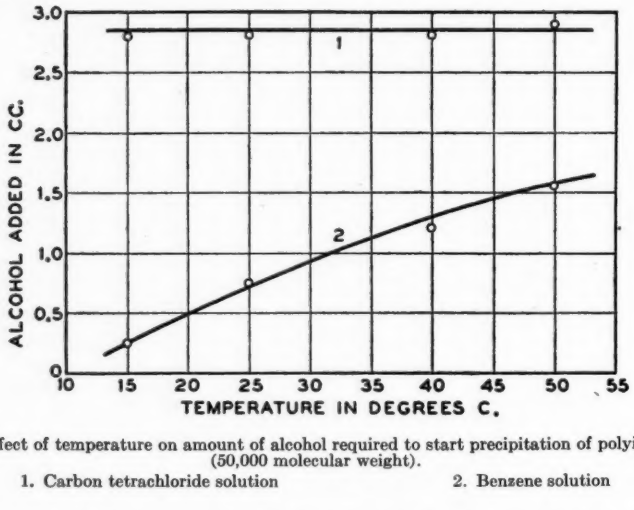

FIG. 7.—Effect of temperature on amount of alcohol required to start precipitation of polyisobutylene (50,000 molecular weight).

1. Carbon tetrachloride solution 2. Benzene solution

EFFECT OF SHAKING ON VISCOSITY OF POLYISOBUTYLENE SOLUTIONS

Thomas and his coworkers[3] found extremely large effects of shaking on the viscosity of *n*-heptane solutions of high polymers of isobutylene. Observations made on finely cut samples of high-polymeric polyisobutylene in chlorofrm and *n*-hexane to make 0.084 per cent solutions showed that, after 5 hours at room temperature, the polymer was highly swollen, and after 48 hours it apparently was completely dispersed by diffusion. To show the effect of shaking, fully dispersed high-polymer solutions were prepared in *n*-hexane and allowed to stand 5 days. After the viscosities were measured the solutions were shaken vigorously for 5 minutes and the viscosities were redetermined. These results, given in Table VIII, show that shaking affects only the highest polymer.

TABLE VIII

EFFECT OF SHAKING *n*-HEXANE SOLUTIONS OF POLYISOBUTYLENE ON VISCOSITY

Polymer[a]	Solvent used	Concn. (base molal)	Shaking period (min.)	η_r	Mol. wt. = $\log \eta_r \times 0.75 \times 10^4 C$
A	*n*-Hexane	0.0500	0	2.130	31,950
			5	2.130	31,950
B	*n*-Hexane	0.0250	0	2.191	102,000
			5	2.172	101,000
C	*n*-Hexane	0.0150	0	2.118	163,000
			5	1.880	137,000

[a] Commercial polymers kindly supplied by G. P. Mack, Advance Solvents and Chemicals Corporation.

Almost identical results were obtained by employing chloroform as a solvent. This confirms the work of Thomas and associates, who presented evidence to indicate that the polymer chains had been broken as a result of shaking. Possibly the reduction in viscosity of the high polymer solution upon shaking is a molecular aggregation effect.

In view of these results it is clear, as pointed out in the case of rubber[13], that solutions of high polymers should not be prepared by violent shaking, but by allowing them to stand long enough to obtain complete diffusion of the polymer into the solvent and then gently shaking before viscosity measurements are made.

FRACTIONATION OF HIGH-MOLECULAR ISOBUTYLENE POLYMER

A study of fractionating natural crude rubber[11] showed the efficacy of the diffusion method when a poor solvent, such as a mixture of hexane and acetone, was employed. A similar study was carried out on a commercial polyisobutylene. A polymer weighing 25 grams was covered with 500 cc. of a mixture of equal volumes of *n*-hexane and acetone, and allowed to stand 48 hours or longer. The solvent was decanted from the swollen polymer, and the solvent was evaporated to determine the amount of polymer which had diffused into it. The viscosity of this extract in *n*-hexane was also determined. As extraction progressed, the proportion of hexane in the mixture was increased and the operation repeated. The course of the extraction and the data on viscosity–molecular weight of the fractions are given in Table IX.

TABLE IX

FRACTIONATION OF POLYISOBUTYLENE

Fraction no.	Hexane-acetone ratio	Total extn. period (days)	Percentage of original material	Average mol. wt.
1, 2	50-50 to 52-48	6	4.0	630
3, 4, 5	54-46 to 58-42	7	1.3	1,650
6, 7, 8, 9	60-40 to 66-34	8	1.9	2,600
10, 11, 12	68-32 to 72-28	6	1.8	6,100
13, 14	74-26	6	12.9	36,450
15	74-26	7	11.1	41,700
16	75-25	4	9.8	41,700
17	76-24	4	29.7	41,850
18[a]	....	..	13.1	25,200
19[a]	....	..	13.8	69,800

[a] Residue from fraction 17 dissolved in *n*-hexane and partially precipitated by adding acetone to give fraction 18. Fraction 19 obtained by evaporating the filtrate from fraction 18.

When the hexane-acetone ratio is increased from 72-28 to 74-26, a sharp increase in solvent power occurs. This indicates the need for making more gradual changes in the hexane content in this range to obtain better fractionation. These results show also that, once the solvent mixture reaches a critical solvent power, fractionation by the diffusion method is no longer effective.

The final fractionation was carried out by dissolving the residual polymer in *n*-hexane and partially precipitating it with acetone. These data and those for the lower polymers illustrate, as in the case of rubber, that a combination of fractional diffusion and partial precipitation is effective as a fractionating procedure for polyisobutylene.

CONCLUSIONS

1. The cryoscopic method is not satisfactory for polyisobutylenes having chain lengths much over 40 isobutylene units, on account of the failure of their solutions to obey Raoult's law.

2. The present work has led to the selection of a K_{cm} value of 0.75×10^4 for *n*-hexane solutions of polyisobutylene for use in the equation $M = (\log \eta_r \times K_{cm})/C$.

3. Extrapolation of cryoscopic data obtained on nonideal solutions to infinite dilution gives inordinately high molecular weight values compared with those based on freezing point measurements of ideal solutions.

4. Of several solvents studied, *n*-hexane was found to be the best for viscosity–molecular weight measurements of polyisobutylene.

5. Fractionation of polyisobutylene by diffusion into mixtures of *n*-hexane and acetone resulted in the separation of the lower polymer fractions.

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THE AUTOÖXIDIZABILITY OF THE ALKYL GROUPS IN XYLENE *

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In the course of early experiments on the oxidation of rubber, it was observed that its solutions in commercial xylene, when exposed at 75° to a stream of oxygen, in presence of acetic anhydride (added to accelerate reaction) and a cobalt catalyst, gave *m*- and *p*-toluic acid, together with neutral liquids which were clearly not derived from the rubber. For instance, when a solution of 675 g. of rubber in 6075 g. of xylene was mixed with 844 cc. of acetic anhydride and 42 g. of cobalt naphthenate, and the mixture (in 4 batches) was treated at 75° for 2 days with a stream of oxygen, there were obtained, respectively, (1) by extraction of the xylene solution with 10% caustic alkali and (2) by subsequent distillation at approximately 1 mm. pressure of the volatile product from the residual xylene liquor, about 10 g. of crystalline acid and 80 g. of volatile neutral oxidation products. The acid was toluic acid (found: C, 70.6; H, 6.1; equiv., 135; calculated for $C_8H_8O_2$: C, 70.55; H, 5.95%; equiv. 136), from which samples of both the *m*- and the *p*-isomeride (m. p. 110° and 176°, respectively) were isolated by fractional crystallization. The neutral products when fractionally distilled gave: (1) aldehydic material, b. p. 85—87°/15 mm. (21 g.); (2) aldehydic material, b. p. 87—105°/15 mm. (13 g.); (3) alcoholic material, b. p. 105—108°/15 mm. (41 g.); and (4) neutral material, b. p. > 108°/15 mm. (5 g.). Fraction (1) was nearly pure tolualdehyde (found: C, 61.3; H, 6.15; calculated for C_8H_8O: C, 61.0; H, 6.25%), and gave at once a mixture of isomeric semicarbazones, m. p. 205°; also it gave on oxidation with excess of boiling alkaline permanganate an 80% yield of mixed phthalic acids (found: C, 58.0; H, 3.55; calculated for $C_8H_6O_4$: C, 57.8; H, 3.65%). From the methyl ester derived from the mixed acids, methyl terephthalate, m. p. 139°, and methyl isophthalate, m. p. 65°, were easily separated. Fraction (3), doubtless consisting of impure tolyl alcohols (found: C, 75.4; H, 7.7; calculated for $C_8H_{10}O$: C, 78.65; H, 8.25%), gave, on oxidation with boiling permanganate, good yields of mixed phthalic acids, resolvable after esterification into the *m*- and the *p*-isomeride.

When xylene (200 cc.) containing no dissolved rubber was similarly oxidized for 1 day at 75° in presence of cobalt naphthenate (1 g.) and acetic anhydride (25 cc.), there was obtained a quite similar mixture (14.5 g.) of the liquid and the acid oxidation products.

This oxidation of xylene, which is facilitated by the cobalt catalysts employed, doubtless proceeds *via* the hydroperoxide, $CH_3C_6H_4CH_2OOH$.

* Reprinted from the *Journal of the Chemical Society*, **1942**, page 185.

SOLVATION IN DISPERSED SYSTEMS. XII

INFLUENCE OF SURFACE-ACTIVE SUBSTANCES ON THE STRUCTURE OF RUBBER FRACTIONS *

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We have previously shown that the addition of nitrogen-containing compounds to sols of butadiene polymers results in the development of colloidal structures. To explain the mechanism of this action, the effect of adding similar compounds to fractions of crude rubber of varying degrees of aggregation was studied.

These active substances, when dissolved either in low molecular weight fractions of the polymer or in a mutual dispersing medium, become adsorbed on the rubber micelles, change the equilibrium between the fractions, and modify the properties of the colloid. The molecular nature of the dispersing medium has a marked effect on the interaction between the polymer and the active substances. The data obtained by us are shown in Table I.

Table I

Percentage Yields of Rubber Fractions in the Presence of *p*-Nitrosodimethylaniline

Concentration of *p*-nitrosodimethylaniline (in percentage on the polymer)	Fraction I		Fraction II		Fraction III	
	From toluene	From pentane	From toluene	From pentane	From toluene	From pentane
0 (pure polymer)	26	42	35	19	2.7	
0.87	10	40	46	27	11	Does
1.74	7.0	39	42	18	23	not
2.61	31.0	30	45	22	5	separate

p-Nitrosodimethylaniline sharply increases the yield of less aggregated fractions, and thus appears to be a peptizing agent for the more highly aggregated portions of the polymer. The extent of this effect on the displacement of the equilibrium between the fractions depends on the nature of the solvent. In pentane the polymer is more aggregated, the micelles are more compact, and the total inner surface of the sol is smaller than it is in toluene solution. The addition of *p*-nitrosodimethylaniline shows, therefore, a smaller effect in pentane than in toluene.

It can be shown that the curve relating the yield of a fraction to the concentration of the active ingredient has a clearly defined point of inflection. This maximum activity is a general characteristic of surface-active substances, and is manifest by changes in viscosity, critical yield point and other properties of the rubber sol.

The properties of individual fractions can be characterized conveniently by the relative viscosities of their solutions. Table II shows the relative viscosities η_{rel} of 2 per cent solutions of sol fractions in toluene, and the changes in relative viscosity on addition of the active substance (Figure 1).

* Translated by L. Talalay for Rubber Chemistry and Technology from *Colloid Journal* (U.S.S.R.) 6, 761–763 (1940).

TABLE II

RELATIVE VISCOSITIES OF THE SOLS OF FRACTIONS OF THE POLYMER[1]

Concentration of *p*-nitrosodimethylaniline (in percentage on the polymer)	Fractions			
	I from toluene	II from toluene	III from toluene	I from pentane
0 (pure polymer)	9.6	3.0	1.2	7.0
0.87	7.0	4.0	3.2	5.4
1.74	6.8	4.6	4.0	5.2
2.61	4.0	5.6	(2.1)	9.2

[1] Fractions are obtained by fractional precipitation with ethyl alcohol. Increasing amounts of alcohol are used to precipitate successively fractions I, II and III.

The data in Table II are interesting. The addition of compounds containing active nitrogen, in particular *p*-nitrosodimethylaniline, affects fractions of various states of aggregation in different ways. The most highly aggregated fractions (I) are evidently peptized by *p*-nitrosodimethylaniline; the less aggregated fractions (II and III) are rendered colloidal, and this results in the entire system becoming colloidal.

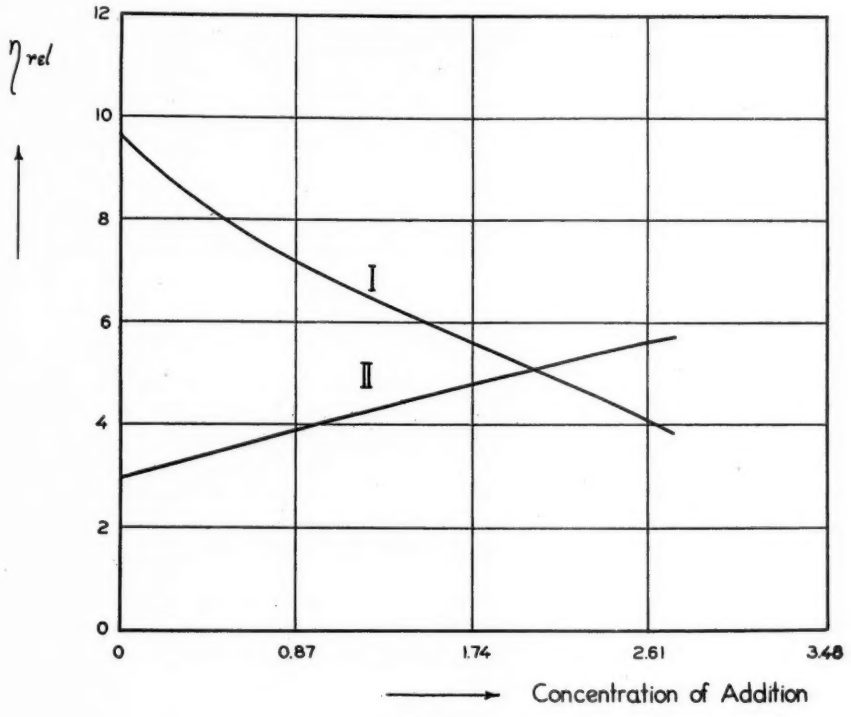


FIG. 1.

Assuming this, it is possible to explain the increase in yield of fraction II (Table I) in the presence of *p*-nitrosodimethylaniline, and the accompanying increase in the critical yield point of the sol. As a result of the interaction of the active additions with the polymer, more of the colloidal fractions are

formed. Fraction II, which separates on the addition of the active reagents, is characterized by a higher state of aggregation than fraction II, which separates from the pure polymer.

The mechanism of the interaction of surface-active, nitrogen-containing compounds with the polymer cannot be said to be fully understood. Assuming that a chemical reaction occurs, we can say that the nature of the reaction depends on the state of aggregation of the various fractions. The probability of either a surface or volume reaction taking place varies within rather wide limits, so that the actual character of the reaction with various fractions can be quite different. It would be reasonable to assume that the probability of a volume reaction taking place is greater for less aggregated fractions, in which case the chains have greater freedom of movement.

From the experimental data presented, we can draw the conclusion only that compounds containing surface-active nitrogen, when added to a sol, act as peptizing agents for fractions with well developed colloidal structures, yet at the same time are capable of assisting in the development of definite structures in systems with low states of aggregation.

THE INTERACTION BETWEEN RUBBER AND LIQUIDS

1. A THERMODYNAMICAL STUDY OF THE SYSTEM RUBBER–BENZENE *

G. Gee and L. R. G. Treloar

A complete thermodynamic description of a binary system involves the expression of the volume, free energy and heat content of the system in terms of composition, temperature and pressure. In no single case has this been done for a mixture of a high-polymeric material with a low-molecular liquid, the only data usually available being the partial molar free energy of dilution over a part of the concentration range at a single temperature. This quantity can be calculated for rubber + benzene from the vapor pressure data of Lens[1] and Stamberger[2] and from osmotic and swelling pressures measured by various workers[3], but most of these results are of doubtful accuracy. Further, the range of composition thus covered is by no means complete, and no reliable temperature coefficients have been recorded. It is the object of this paper to provide much more complete data for a typical system.

FUNDAMENTAL THEORY

Before describing our experimental methods and results, it is desirable to review briefly how the free energy and heat content may be obtained from vapor pressure measurements[4].

Gibbs' Free Energy and Heat of Dilution

We consider the isothermal transfer of 1 gram of liquid from a mass of pure liquid of vapor pressure p_0° to an infinite amount of a rubber-liquid mixture above which the vapor pressure of the liquid is p_0^m. The two phases will be denoted by indices $^\circ$ (pure liquid) and ^{m} (mixture), and the components by subscripts $_0$ (pure liquid) and $_r$ (rubber). The "Gibbs' free energy of dilution" is defined as the resultant increase Δg_0 in the Gibbs' free energy of the whole system; the "heat of dilution" as the increase Δh_0 in the heat content of the system.

Since the partial molar Gibbs' free energy G_0^m of the liquid in the mixture is numerically equal to its chemical potential μ_0^m [5], the increase g_0^m in the Gibbs' free energy of the mixture due to the addition of 1 gram of solvent is given by:

$$g_0^m = \frac{\mu_0^m}{M_0} \tag{1}$$

where M_0 is the molecular weight of the liquid. Similarly, the increase $-g_0^\circ$ in the Gibbs' free energy of the liquid due to the removal of 1 gram of liquid is

* Reprinted from the *Transactions of the Faraday Society*, Vol. 38, pages 147–165, April 1942.

$-\frac{\mu_o^\circ}{M_o}$. Hence the Gibbs' free energy of dilution is:

$$\Delta g_o = g_o^m - g_o^\circ = \frac{1}{M_o}(\mu_o^m - \mu_o^\circ) \tag{2}$$

Now, the chemical potential μ of a perfect gas at a pressure p can be written in the form[6]:

$$\mu = \mu^\circ(T) + RT \ln p \tag{3}$$

where $\mu^\circ(T)$ is a function only of temperature. This equation may be applied to the vapors above both the pure liquid and the mixture, provided that the vapor behaves as a perfect gas, a condition which holds to a close approximation except in the neighborhood of the critical point. Further, since the condition for the equilibrium of a component between two phases is that its chemical potential shall be the same in both phases, we may write for the chemical potentials of the liquid in the mixture and in the pure liquid:

$$\left.\begin{aligned} \mu_o^m &= \mu_o^\circ(T) + RT \ln p_o^m \\ \mu_o^\circ &= \mu_o^\circ(T) + RT \ln p_o^\circ \end{aligned}\right\} \tag{4}$$

Substituting in (2) gives at once the required relationship:

$$\Delta g_o = \frac{RT}{M_o} \ln p_o^m/p_o^\circ \tag{5}$$

When the proportion of rubber is low, the vapor pressure lowering is too small to measure directly, but it can still be calculated from the osmotic pressure or swelling pressure of the mixture. These two quantities are thermodynamically identical, for both may be defined as the hydrostatic pressure which must be applied to the mixture to bring it into osmotic equilibrium with pure liquid. To derive a relationship between the osmotic pressure of the mixture and its vapor pressure, we consider the osmotic equilibrium between two phases $^\circ$ and ^{m} separated by a membrane permeable only to the liquid. The condition for equilibrium is, from (4), that $p_o^\circ = p_o^m$. We now keep the temperature and pressure of the liquid fixed, and vary the pressure P^m and composition w_r[7] of the mixture isothermally so as to maintain equilibrium. For all such changes we may write:

$$d \ln p_o^m = \left(\frac{\partial \ln p_o^m}{\partial P^m}\right)_{w_r} dP^m + \left(\frac{\partial \ln p_o^m}{\partial w_r}\right)_{P_m} dw_r = 0 \tag{6}$$

Further, by Equation (4):

$$\left(\frac{\partial \ln p_o^m}{\partial P^m}\right)_{w_r, T} = \frac{1}{RT}\left(\frac{\partial \mu_o^m}{\partial P^m}\right)_{w_r, T} = \frac{V_o^m}{RT}^{8} \tag{7}$$

where V_o^m is the partial molar volume of the liquid in the mixture. Substituting from (7) in (6) and integrating:

$$\int_{P^o}^{P^m} (V_o^m)_{w_r} dP = -RT \int_o^{w_r} \left(\frac{\partial \ln p_o^m}{\partial w_r}\right) dw_r \tag{8}$$

where P^o is the hydrostatic pressure above the pure liquid. If we write

$P^m - P^o = \Pi$ and $[V_o^m]$ for the value of V_o^m at a pressure $= P^o + \frac{1}{2}\Pi$, Equation (8) gives at once as an approximation for the osmotic pressure:

$$\Pi \backsimeq \frac{RT}{[V_o^m]} \ln p_o^o/p_o^m \tag{9}$$

in which p_o^m and p_o^o are both to be measured at the same pressure, say P^o. Since Equation (9) is to be employed only for the calculation of the relative vapor pressures of dilute solutions, Π will be small and $[V_o^m]$ may be replaced by V_o^m, its value at atmospheric pressure.

Combining with (5):

$$\Delta g_o \backsimeq \frac{\Pi V_o^m}{M_o} \tag{10}$$

The heat of dilution has now to be obtained from the temperature coefficient of the Gibbs' free energy. The partial molar heat contents of the liquid in the two phases are given by[9]:

$$\left.\begin{aligned} H_o^m &= \left(\frac{\partial \mu_o^m/T}{\partial 1/T}\right)_{P, w_r} \\ H_o^o &= \left(\frac{\partial \mu_o^o/T}{\partial 1/T}\right)_{P, w_r} \end{aligned}\right\} \tag{11}$$

We then have:

$$\Delta h_o = \frac{1}{M_o}(H_o^m - H_o^o) \tag{12}$$

and by combining with (2) and (5):

$$\Delta h_o = \left(\frac{\partial \Delta g_o/T}{\partial 1/T}\right)_{P, w_r} = -\frac{RT^2}{M_o}\left(\frac{\partial \ln p_o^m/p_o^o}{\partial T}\right)_{P, w_r} \tag{13}$$

Gibbs' Free Energy and Heat of Solution

We now consider the isothermal transfer of 1 gram of rubber from a mass of pure rubber to an infinite amount of a rubber-liquid mixture. The "Gibbs' free energy of solution" is defined as the resultant increase Δg_r in the Gibbs' free energy of the whole system; the "heat of solution" as the increase Δh_r in the heat content of the system. These quantities are calculable from the Gibbs' free energy and heat of dilution by making use of the Gibbs-Duhem equation[10] in the modified form:

$$\left.\begin{aligned} \Delta g_r &= -\int \frac{1 - w_r}{w_r} \mathrm{d}\Delta g_o \\ \Delta h_r &= -\int \frac{1 - w_r}{w_r} \mathrm{d}\Delta h_o \end{aligned}\right\} \tag{14}$$

Entropy of Dilution and Solution

The entropy increases associated with the two processes considered are obtained at once from the heats and Gibbs' free energies:

$$\left.\begin{aligned} \Delta g_o &= \Delta h_o - T\Delta s_o \\ \Delta g_r &= \Delta h_r - T\Delta s_r \end{aligned}\right\} \tag{15}$$

EXPERIMENTAL PROCEDURE AND RESULTS

From the above equation, all the thermodynamic functions required may be calculated from vapor pressure data. The Gibbs' free energy of dilution is obtained from Equation (5); the heat of dilution from Equation (13), and the entropy of dilution from Equation (15). Equation (14) then gives the corresponding solution functions.

The general problem was, therefore, to determine the relative vapor pressure p_o^m/p_o°, and the temperature coefficient of p_o^m/p_o° over as wide a range of composition w_r as possible. No single method is capable of covering an adequate range, and four methods have therefore been employed, *viz.*: (1) direct manometric measurement of vapor pressure, covering the range 0.05 to 0.98 in p_o^m/p_o°, (2) extension to lower relative vapor pressures by the use of a McLeod gauge (p_o^m/p_o° from 0.003 to 0.06), (3) equilibration between rubber solution and solution of known vapor pressure ($(p_o^\circ - p_o^m)/p_o^\circ$ from 0.0005 to 0.02), and (4) osmotic pressure measurements ($(p_o^\circ - p_o^m)/p_o^\circ$ from $2 \times 10^{-6} \times$ to $2\ 10^{-4}$).

Materials.—Most of the work was carried out on an intermediate fraction of rubber hydrocarbon prepared by the methods of Bloomfield and Farmer[11], but, in the high vapor pressure region, measurements were also made on a lower fraction (extracted by a mixture of 55% petroleum ether and 45% acetone, referred to below as 55/45 Fraction) and on two samples of thermally degraded rubbers kindly prepared for us by J. L. Bolland[12]. The benzene used was of AnalaR grade, purified either by recrystallization or by distillation.

Direct Manometric Method

The apparatus employed is shown in Figure 1. The bulb R contained the rubber (0.1 g.), and the side-tube B a quantity of mercury. A thick-walled glass tube sealed on at C provided connection to the vacuum line. After

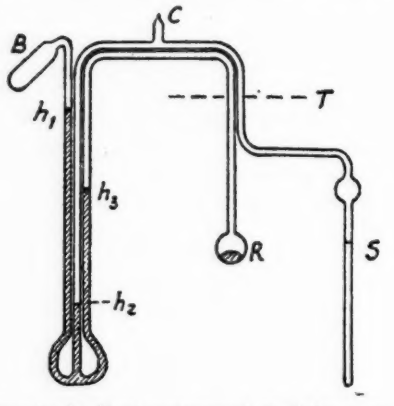


Fig. 1.—Apparatus for direct measurement of relative vapor pressures.

strongly heating the glass parts and boiling the mercury, the rubber was heated at 100° C for one hour to remove dissolved gas, evacuation being effected by means of a mercury diffusion pump. The mercury in B was then poured out into the manometer tubing (by bending the glass tube above C), thus isolating the rubber, and benzene was distilled *in vacuo* into the calibrated tube S, after

which the system was sealed off at C. To transfer benzene on to the rubber, communication between R and S was established by pouring the mercury back into B (after first freezing out vapor by applying liquid air). When the desired amount has been transferred, liquid air was applied to R and S, and the mercury replaced. The amount of liquid transferred was determined from the change in height of the meniscus in S, the measurement being made with S immersed up to the liquid level in a bath at a temperature below room temperature (15° C) to prevent condensation of liquid on the internal walls of the tubing. Correction was made for the amount of benzene present as vapor above the mixture, so as to obtain the amount in the rubber-benzene mixture.

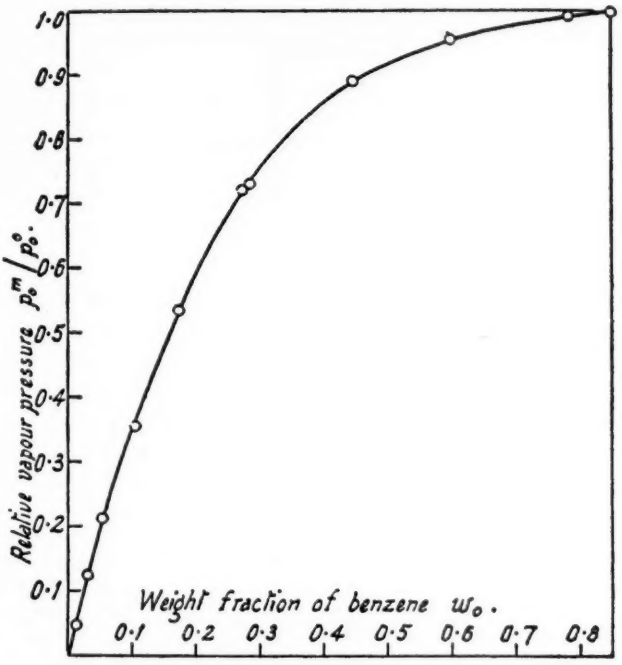


FIG. 2.—Relative vapor pressures of rubber-benzene mixtures by direct manometric method. Intermediate fraction, 25° C.

R and S were then immersed in the thermostat to the level T, the manometer and remaining tubing, which was outside the thermostat, being kept at a slightly higher temperature by an electric heater wound round the glass, and time was allowed for equilibrium to be attained. A period of a few hours was generally sufficient, but at least sixteen hours was normally allowed before taking readings. Since B was evacuated, $h_1 - h_2$ was the vapor pressure of the pure benzene, and $h_1 - h_3$ the vapor pressure above the rubber-benzene mixture.

Figure 2 shows the vapor pressure curve at 25° C obtained in this way, the ordinates being the relative vapor pressure p_o^m/p_o° and the abscissæ the weight fraction of benzene in the mixture. The curve obtained was not dependent on whether the benzene concentration was being increased or decreased, *i.e.*,

there were no hysteresis effects. Work on this part of the vapor pressure curve has already been done by Stamberger[2] and by Lens[1].

Temperature Coefficient

A preliminary experiment was carried out at a temperature of 40° C. The differences between the vapor pressures at this temperature and at 25° C were hardly greater than the experimental errors. This showed the necessity of using a much larger temperature interval for the determination of the temperature coefficient, and the apparatus was therefore modified, as shown in Figure 3, to enable an upper temperature of 100° C to be used. The high

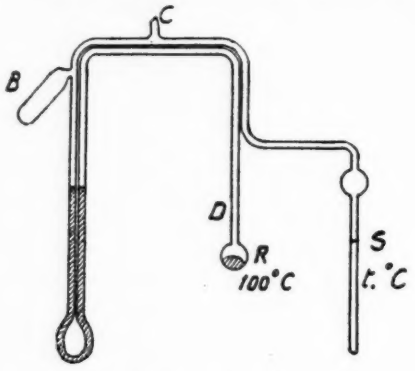


Fig. 3.—Temperature coefficient of vapor pressure.

vapor pressure of benzene at 100° C (1378 mm.) made it impracticable to retain the vacuum limb of the manometer, and the bulb B containing mercury was placed in the position shown. The rubber was degassed at 150° C for one hour. After measuring the difference in the vapor pressure in the usual way at 25° C, R and S were gradually heated so as to maintain an approximate pressure balance, until R finally reached 100° C. S was then maintained at a temperature (t°) such that the pressure on each side of the manometer was the same. Under these conditions the vapor pressure of the rubber-benzene mixture at 100° C was equal to the saturation vapor pressure of benzene at t° C. The latter was determined from an independent experiment, as was also p_o° at 100° C. The volume of the bulb R and its connecting tubing was kept as small as possible so as to reduce to a minimum the correction for the mass of vapor above the mixture. Using 1 gram of rubber, this correction amounted at most to 5 per cent of the benzene admitted to the rubber.

For each of the benzene concentrations, the relative vapor pressure was determined both at 25° and at 100° C. Since the amount of vapor in the space above the mixture was greater at the higher temperature, it was necessary to apply a correction to be able to compare the relative vapor pressures at the same concentrations of benzene in the mixture. This was readily done by using the already determined slope of the vapor pressure/concentration curve. The results obtained are given in Table I.

In the above experiment, error may arise from the fact that, owing to the presence of impurities, the liquid distilled over on to the rubber may have a slightly higher vapor pressure than that remaining in the tube S, and a similar

error may occur in the separate determination of the vapor pressure of the pure benzene at elevated temperatures. This is the reason why the total error in the determination of vapor pressure was so large a fraction of the difference being measured.

TABLE I

TEMPERATURE COEFFICIENT OF VAPOR PRESSURE

w_2	$p_0^m/p_0°$ 25°	$p_0^m/p_0°$ 100°	% Difference (referred to 100° value)
0.0545	0.2009	0.1874	7.2 ± 3
0.0836	0.283	0.266	6.4 ± 3
0.2212	0.625	0.595	5.0 ± 3
0.411	0.855	0.849	0.7 ± 3

REGION OF LOW VAPOR PRESSURES. 25° AND 100° C

The direct measurement of p_0^m becomes inaccurate when it is less than 10 mm., and a more sensitive method of measuring these pressures had to be sought. The arrangement adopted is shown in Figure 4. In it was incor-

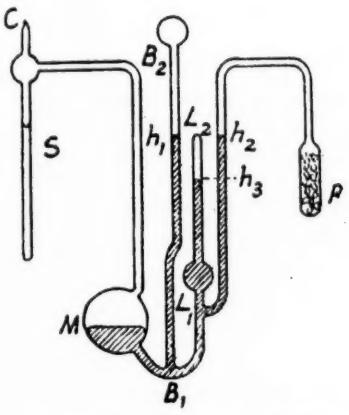


FIG. 4.—Apparatus incorporating McLeod gauge for measurement of low vapor pressures.

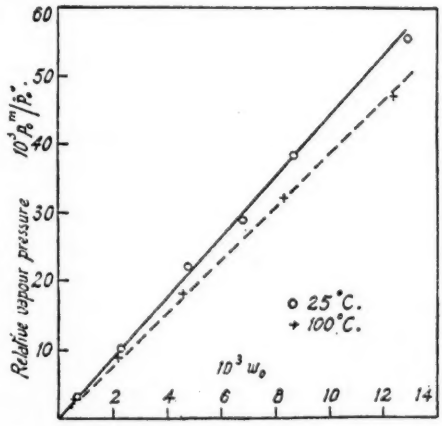


FIG. 5.—Relative vapor pressures of rubber-benzene mixtures at low concentrations of benzene. Intermediate fraction.

porated a relatively insensitive McLeod gauge, consisting of the bulb and stem L_1L_2 and the vacuum capillary B_1B_2, which covered a range of pressures from 0.1 mm. to 6 mm. The rubber (1.4 g.) was in R, and mercury in the reservoir M. The rubber was degassed at 150° C for one hour, after which treatment the gauge indicated no appreciable evolution of gas on subsequently heating to 100° C. The solvent tube S was filled with benzene in the usual way, and the apparatus was sealed off at C.

To connect the benzene tube S with R, the mercury was poured out into M, L_1L_2 being then horizontal; when the apparatus was restored to the vertical position the connection was broken. The operation of the gauge was as follows: Application of liquid air to S caused the mercury levels h_2 and h_3 to fall to M, thus permitting the vapor in contact with R to fill the gauge L_1L_2.

This position was maintained until the attainment of equilibrium, with R kept at the requisite temperature (25° or 100° C). To take a pressure reading the temperature of S was raised to 25° C, at which the vapor pressure of the solvent was just sufficient to raise the mercury level in B to the position h_1 in Figure 4. Pressures in excess of 6 mm. were read directly by comparing h_1 and h_2.

The use of the McLeod gauge involves the assumption that Boyle's law can be applied to benzene vapor in the region of temperatures and pressures encountered in these experiments. A test of this assumption was made by replacing R by a large bulb (300 cc.) into which known quantities of benzene were introduced from S. The pressures calculated on the basis of the simple gas laws were found to agree with the measured pressures to within 3 per cent at 6 mm., this difference being comparable with the other errors involved in the measurement.

The values of p_o^m/p_o° at 25° and 100° C obtained with this apparatus are plotted against the solvent concentration in Figure 5. In this region the relationship between vapor pressure and concentration appears to be approximately linear down to a solvent concentration of less than 0.1 per cent, *i.e.*, in effect down to zero concentration, so that the temperature coefficient is approximately constant. From the slopes of the two lines in Figure 5, the increase in p_o^m/p_o° between 100° and 25° is 14 per cent.

Equilibration of Rubber and Triolein Solutions

The direct manometric measurement was again inapplicable when p_o^m/p_o° approached unity, *i.e.*, for values of $(p_o^\circ - p_o^m)/p_o^\circ$ of less than about 0.02. To extend the vapor pressure measurements to very much higher solvent concentrations, the method adopted was to allow the rubber solution in a bulb A (Figure 6(*b*)) to come into equilibrium with a solution of triolein in benzene

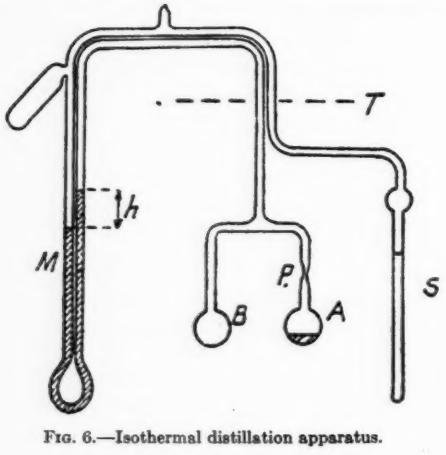
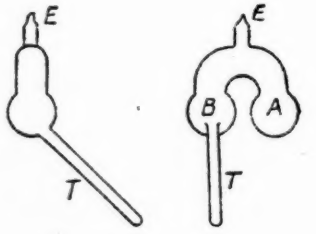


Fig. 6.—Isothermal distillation apparatus.



(*a*) Side elevation (*b*) Front elevation

Fig. 7.—Vapor pressures of triolein solutions.

in bulb B. In the equilibrium condition, the vapor pressures of the two solutions were equal; hence, by measuring the concentrations of the two solutions, and calculating the lowering of vapor pressure due to the triolein, the relative vapor pressure of the rubber solution could be determined. This required a

preliminary investigation into the properties of triolein solutions, which will now be considered.

The measurement of the vapor pressure lowering ($\Delta p_o/p_o$) for triolein solutions made use of the apparatus shown in Figure 7. A known weight of triolein was placed in bulb A, into which a measured amount of benzene was distilled from the tube S. The pressure difference, h_1, was measured on the manometer M when A, B and S were maintained at 45° C. The whole of the solvent in A was then distilled over into B, and A (with the triolein) was sealed off at P. On reinsertion in the thermostat, the pressure difference was not in general zero, as it would be if the benzene were absolutely pure, but there was a residual pressure h_2 representing a vapor pressure difference between the benzene in B and that in S. The required vapor pressure lowering Δp_o due to the triolein was $h_1 - h_2$, which was thus measured by reference to the particular sample of solvent actually present in the solution. The experimental data are given in Table II. If the solution were ideal, the vapor

TABLE II

Conc. $\frac{\text{g. triolein}}{\text{g. solution}}$	$\Delta p_o/p_o^\circ$	$1 - N_o$	$\ln f$	$\frac{\ln f}{(1 - N_o)^2}$
0.154	0.0220	0.0158	0.0064	25.6
0.267	0.0513	0.0311	0.0211	21.8
0.369	0.096	0.0490	0.0507	21.1
0.439	0.141	0.0636	0.0863	21.4
			Best value	21.5

pressure lowering would be related to the mole fraction of benzene in the solution (N_o) by Raoult's Law:

$$\Delta p_o/p_o^\circ = 1 - N_o.$$

The differences between the figures in columns 2 and 3 represent the departures from ideality. As a basis for extrapolation to lower concentrations of triolein, an activity coefficient f_o, defined by the relation:

$$\Delta p_o/p_o^\circ = 1 - N_o f_o$$

is introduced, the calculated values of $\ln f_o$ appearing in column 4. For many solutions showing only small departures from ideality, it is found that $\ln f_o = \text{const.}\ (1 - N_o)^2$ [13]; this relationship represents the above results with reasonable accuracy, as shown in column 5. The extrapolation of $\Delta p_o/p_o^\circ$ to lower concentrations involves no important uncertainty, because the correction introduced by the coefficient f_o rapidly becomes smaller with diminishing concentration of triolein, and is negligible when $\Delta p_o/p_o^\circ < 0.001$.

The details of the apparatus devised for the experiments with rubber are shown in the front and side elevation drawings of Figure 6. It consisted of two bulbs A and B, one of which carried a calibrated side-tube T at the angle shown. Weighed amounts of triolein and rubber were placed in A and B respectively, and the apparatus was sealed at E to the stem D in Figure 3 in place of the bulb R, benzene being distilled into S in the usual way before sealing the apparatus off at C. A measured quantity of benzene was then transferred from S to A and the bulbs A and B were sealed off at E. The apparatus (Figure 6) was then immersed in the thermostat at 45° C, with the side-tube T horizontal to permit the benzene to distribute itself between the

rubber and triolein. The amount of benzene on the triolein was measured daily (by bringing T into the vertical position and measuring the height of the triolein solution in it) until no further change occurred. Excess solvent was then transferred to B (from A), and equilibrium was approached from the opposite direction. The equilibrium concentrations thus obtained showed close agreement with each other.

From the known volume of benzene on the triolein and the total quantity of benzene admitted to A and B together, the amount on the rubber was obtained by difference (after allowing for vapor), assuming no volume change to occur on mixing benzene and triolein. Hence both the concentration of the rubber solution and its vapor pressure lowering were determined. The data obtained are given in Figure 8.

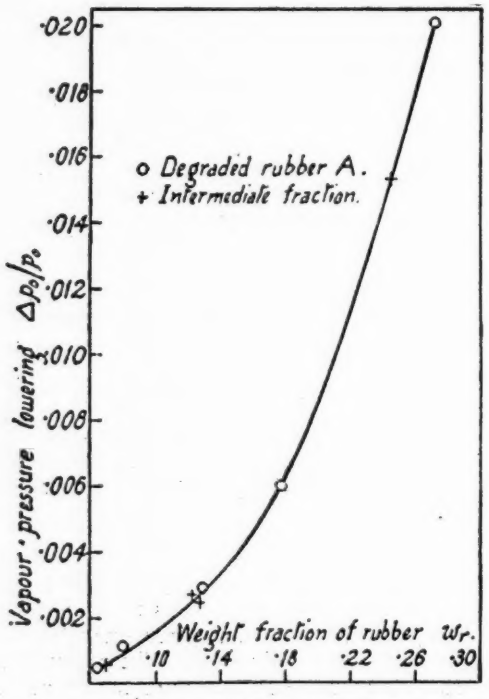


FIG. 8.—Relative vapor pressure lowering of rubber-benzene mixtures by method of isothermal distillation. Temperature 45° C.

The experimental accuracy was insufficient to enable the temperature coefficient of vapor pressure in this region to be obtained.

OSMOTIC PRESSURE MEASUREMENTS

The lowest concentration of rubber which gave a vapor pressure lowering large enough to be measured by the above methods was $w_r \backsimeq 0.07$. To carry the observations further, it was necessary to measure the osmotic pressures of benzene solutions. The osmometer employed, a modification of the one previously described[12], is shown in Figure 9. The membrane (an "ultracellafilter"

as used before) was held vertically between the two cell faces and supported by the grid arrangement C. The upper part of each cell communicated with a glass tube D for the measurement of the pressure head, the lower part with a second chamber fitted with a filling tube E and a screw valve F. In this way it was possible to wash out both cells without dismantling the osmometer. By employing a very fine capillary (approximately 0.2 mm. bore) on the solvent cell, the time required for the attainment of equilibrium was reduced to about 1 to 3 hours, depending on the concentration of the solution. It was, therefore, quite unnecessary to estimate the osmotic pressures by the extrapolation

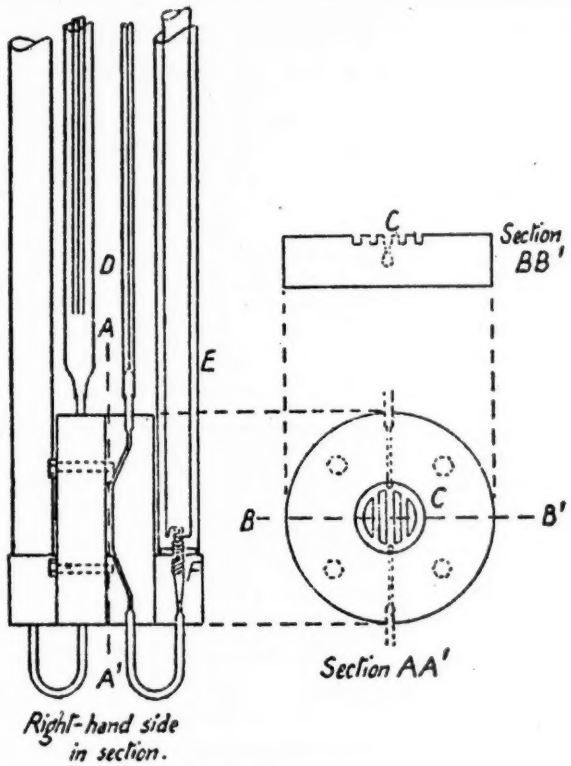


FIG. 9.—The osmometer.

method formerly used, and all data recorded were based on equilibrium values. High osmotic pressures were measured by applying a pressure of nitrogen to the solution. The possible range of measurement is limited at the lower end by the smallest pressures which can be accurately measured, and at the upper end either by the highest viscosity of solution in which an osmotic equilibrium can be established by diffusion or by the highest hydrostatic pressure which can be applied to the membrane without forcing any solute through it. No figures are reported for experiments in which there was evidence of solute passing through the membrane. It is a little difficult to estimate with certainty the probable error of the osmotic pressure measurements. The value obtained depends to some extent on the direction from which equilibrium is

approached. This effect was present in even the most dilute solutions examined, and became serious with highly viscous solutions. The smallness of the error likely to arise at moderate concentrations is illustrated by the following figures for a solution of $w_r = 0.0178_5$. With a rising pressure head an apparent equilibrium was reached at 93.6 mm. benzene. The solution was then agitated, its level reset and equilibrium approached from the other direction, the value found being 96.0 mm. benzene. After further agitation the equilibrium value was again measured with rising pressure and 93.8 mm. obtained. A mean of 94.9 mm. was taken to be correct within 1 per cent. The cause of this behavior is not very clear, but it was not observed when both cells were filled with solvent: successive "blanks" (with measurements intervening) gave

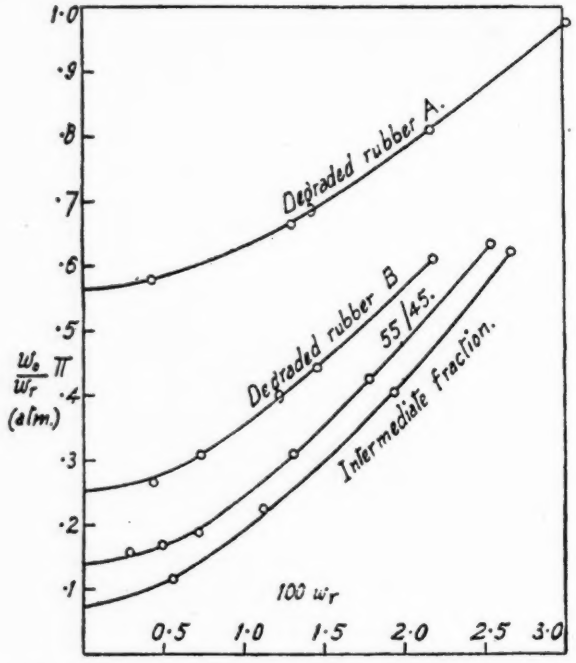


FIG. 10.—Osmotic pressure data for various rubbers. Temperature 25° C.

−64.5, −64.4, −64.7 mm. (This value represents the difference in the capillary rise in the two cells.) At lower concentrations the relative error was more serious, and the absolute error of even the lowest pressures cannot safely be taken as less than 1 mm. of benzene, although it was probably not more than 0.5 mm. Even this lower figure represents 10 per cent of the lowest pressure recorded. Results are given in Figure 10 for two fractions of natural rubber and two thermal degradation products. $\frac{w_o}{w_r}\Pi$ is plotted against w_r, the values of $\left(\frac{w_o}{w_r}\Pi\right)_{w_r \to o}$ being those estimated from measurements in benzene + 15% MeOH[15]. Except in the case of the intermediate fraction the figures were corrected from 30.6° to 25° C by using the temperature coefficients

recorded below. Earlier osmotic measurements[3] do not agree at all closely either among themselves or with the present results.

Temperature Coefficient of Osmotic Pressure

Preliminary measurements showed that the temperature coefficient was too small to measure except under the most favorable circumstances and attention has, therefore, been concentrated on the intermediate concentration range where the relative accuracy was a maximum. Table III gives the measured osmotic pressures and the relative vapor pressures calculated from them.

Table III

$100\ w_r$	t (° C)	100 Π (atm.)	$10^5\ \Delta p_o/p_o°$
	55/45 Fraction		
1.30_5	8.9	0.36_0	1.37
	30.6	0.42_2	1.52
1.78_5	9.9_5	0.70_4	2.65
	30.6	0.79_7	2.87
2.54	9.8	1.52_5	5.7_5
	30.6	1.69	6.1_0
	Degraded rubber B		
2.18	8.9	1.26	4.7_7
	30.6	1.40	5.0_5

The Partial Molar Volume

Equation (10) for the relation between free energy and osmotic pressure contains V_o^m, the partial molar volume of the solvent in the mixture. This quantity is the increase in volume of the mixture when 1 mole of solvent is added to a large volume of the mixture.

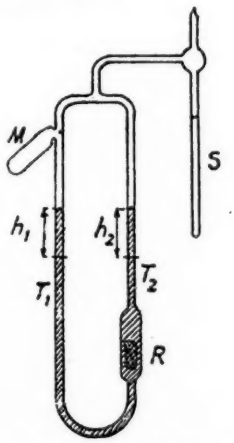


Fig. 11.—Determination of partial molar volumes.

To determine V_o^m experimentally the dilatometer of Figure 11 was employed. The rubber sample R (intermediate fraction) was confined by mercury which reached heights h_1, h_2 above reference marks in the capillary tubes T_1

and T_2. The system was evacuated and benzene admitted to the tube S. To add solvent to the rubber, the mercury was poured into M by tilting the apparatus and replaced when sufficient solvent had distilled over. After time had been allowed for equilibrium to be reached at 25° C, h_1 and h_2 were again observed, together with the change in height of the solvent in S. The increase in volume of the mixture could thus be compared with the volume of benzene added.

TABLE IV

VOLUME CHANGES ON MIXING BENZENE AND RUBBER AT 25° C

w^o	Vol. of benzene added (cc.)	Increase in vol. of mixture (cc.)	Difference %
0.012	0.0077	0.0076	−1.3
0.042	0.0274	0.0262	−4.6
0.142	0.104_2	0.104_8	0.5
0.250	0.206	0.210_5	2.1
0.332	0.301_5	0.306	1.5

TABLE V

HEATS OF DILUTION

w_r	Δh^o Cal./g. benzene Obs.	Eqn. (20)
	Intermediate Fraction	
1 to 0.988	5.0 ± 1	4.5
0.9455	2.7 ± 1	3.4
0.9164	2.4 ± 1	2.9_5
0.7788	1.9 ± 1	1.5
0.589	0.3 ± 1	0.6
	55/45 Fraction	
	$10^4 \Delta h^o$	
$1.30_5 \times 10^{-2}$	1.6 ± 0.8	1.2
$1.78_5 \times 10^{-2}$	2.3 ± 0.5	2.3
2.54×10^{-2}	4 ± 2	4.7
	Degraded rubber B	
2.18×10^{-2}	3 ± 1	3.4

Table IV shows that the increase in volume of the rubber was equal to the volume of solvent added, from $w_o = 0.012$ to 0.332, the partial molar volume of the solvent being thus equal to the molar volume of pure benzene within the limits of accuracy of the present experiments. Experiments by Posnjak[13] also showed that the contraction of total volume on mixing rubber and benzene in proportions varying from 34 per cent benzene to 98 per cent benzene was very small ($< 1\%$). It is evident that in the range covered by the osmotic measurements, V_o^m can be taken as equal to V_o^o.

COMBINATION OF RESULTS OBTAINED BY THE VARIOUS METHODS

We are now in a position to draw the complete vapor pressure-composition curve, extending from pure rubber to infinitely dilute solutions. A direct plot of p_o^m/p_o^o is inconvenient on account of the very wide range covered, and the function chosen to represent the data is $\frac{1}{M_o} \cdot \frac{w_o}{w_r} \cdot \frac{p_o^o - p_o^m}{p_o^m}$, which is positive and finite for all values of w_r. Its extreme limits for the intermediate fraction are 3.5×10^{-6} at $w_r = 0$ and 2.89×10^{-3} at $w_r = 1$. This function has an

intrinsic interest in that it represents the reciprocal molecular weight of a solute which in an ideal solution would give the vapor pressure lowering observed. The four sets of measurements—three vapor pressure regions and the osmotic region—will be seen from Figure 12 to fit together within the limits

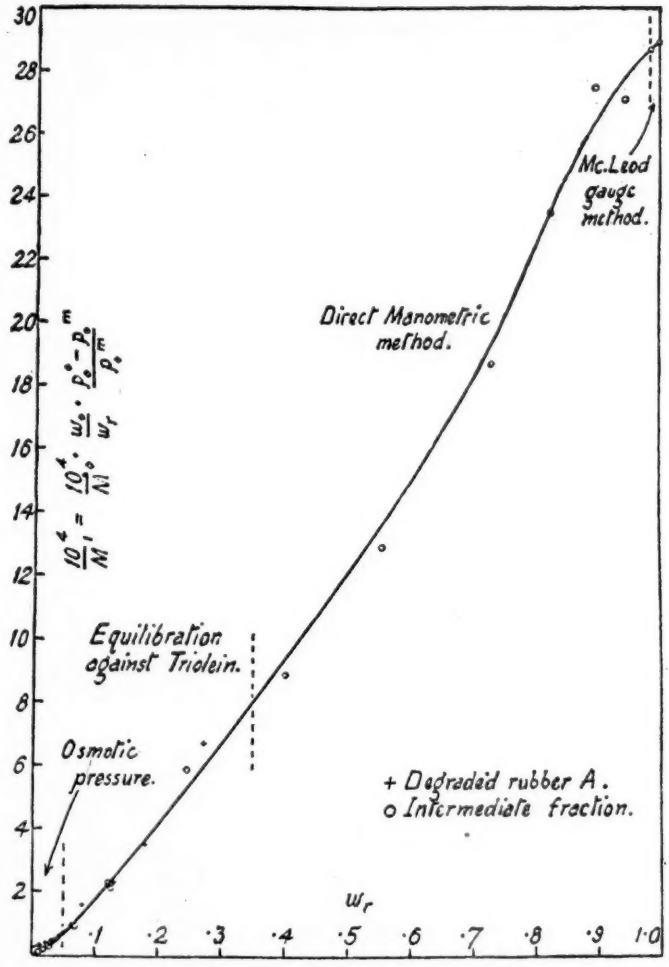


FIG. 12.—Representation of vapor pressure data in terms of apparent molecular weight. Temperature 25° C.

of experimental accuracy[16]. The smooth curve drawn is taken to furnish the best representation of the experimental data.

GIBBS' FREE ENERGIES OF SOLUTION AND DILUTION

The Gibbs' free energy of dilution was calculated by applying Equation (5) to the vapor pressure data, as smoothed in Figure 12. The Gibbs' free energy of solution was then obtained by graphical integration of Equation (14). These quantities are tabulated below (Table VI).

TABLE VI

THERMODYNAMIC PROPERTIES OF RUBBER-BENZENE MIXTURES AT 25° C

w_r	$-\Delta g_o$	Δh_o	$T\Delta s_o$	$-\Delta g_r$	Δh_r	$T\Delta s_r$
0	0	0	0	∞	1.7_8	∞
10^{-6}	2.1×10^{-9}	7×10^{-13}	2.1×10^{-9}	4.4_5	1.7_8	6.2_3
10^{-5}	2.1×10^{-8}	7×10^{-11}	2.1×10^{-8}	4.4_4	1.7_8	6.2_2
10^{-4}	2.1×10^{-7}	7×10^{-9}	2.2×10^{-7}	4.4_4	1.7_8	6.2_2
10^{-3}	2.3×10^{-6}	7×10^{-7}	3.0×10^{-6}	4.4_3	1.7_8	6.2_1
0.005	1.54×10^{-5}	1.8×10^{-5}	3.3×10^{-5}	4.4_3	1.7_7	6.2
0.01	5.6×10^{-5}	7×10^{-5}	1.3×10^{-4}	4.4_2	1.7_7	6.2
0.02	2.4×10^{-4}	2.9×10^{-4}	5.3×10^{-4}	4.4_1	1.7_5	6.1_5
0.03	6.3×10^{-4}	7×10^{-4}	1.3×10^{-3}	4.3_9	1.7_4	6.1_5
0.04	1.24×10^{-3}	1.2×10^{-3}	$2.4_5 \times 10^{-3}$	4.3_8	1.7_3	6.1
0.05	2.10×10^{-3}	1.9×10^{-3}	4.0×10^{-3}	4.3_6	1.7_1	6.0_5
0.07	4.8×10^{-3}	3.7×10^{-3}	8.5×10^{-3}	4.3_2	1.6_8	6.0
0.09	8.9×10^{-3}	6.4×10^{-3}	$1.5_3 \times 10^{-2}$	4.2_7	1.6_5	5.9
0.12	1.78×10^{-2}	1.2×10^{-2}	3.0×10^{-2}	4.1_9	1.6_1	5.8
0.15	3.1×10^{-2}	1.9×10^{-2}	5.0×10^{-2}	4.1_1	1.5_6	5.7
0.18	4.8×10^{-2}	2.9×10^{-2}	7.7×10^{-2}	4.0_2	1.5_1	5.5
0.22	7.8×10^{-2}	4.6×10^{-2}	0.12_4	3.9_0	1.4_5	5.3_5
0.26	0.115	6.7×10^{-2}	0.18_2	3.7_8	1.3_7	5.1_5
0.30	0.169	9.5×10^{-2}	0.26_5	3.6_5	1.3_0	4.9_5
0.35	0.249	0.14	0.39	3.4_8	1.2_0	4.7
0.40	0.36	0.19_5	0.56	3.3	1.1_1	4.4
0.45	0.50	0.27	0.77	3.1	1.0_2	4.1
0.50	0.69	0.36	1.05	2.9	0.9_1	3.8
0.55	0.92	0.48	1.40	2.7	0.8_1	3.5
0.60	1.22	0.63	1.85	2.4_7	0.7_0	3.2
0.65	1.62	0.81	2.43	2.2_2	0.5_9	2.8
0.70	2.17	1.0_4	3.2_1	1.9_7	0.4_8	2.4_5
0.75	2.9	1.3_4	4.2_5	1.6_9	0.37	2.0_5
0.80	4.0	1.7	5.7	1.3_8	0.27	1.6_5
0.85	5.6_5	2.1_5	7.8	1.0_5	0.17	1.2
0.90	8.0	2.7	10.7	0.71	9×10^{-2}	0.80
0.95	12.4	3.5	15.9	0.37	2.5×10^{-2}	0.39
0.96	13.9	3.7	17.6	0.29	1.6×10^{-2}	0.31
0.97	15.9	3.9	19.8	0.22	9×10^{-3}	0.23
0.98	18.8	4.1	22.9	0.14_7	4×10^{-3}	0.15
0.990	23.8	4.3	28.1	0.075	1.1×10^{-3}	0.076
0.994	27.6	4.3_7	32.0	0.045	4×10^{-4}	0.045
0.997	32.9	4.4_3	37.3	0.023	1.0×10^{-4}	0.023
0.999	41.2	4.4_8	45.7	0.0076	1.1×10^{-5}	0.0076
1.000	∞	4.5	∞	0	0	0

HEATS OF DILUTION AND SOLUTION

The heats of dilution Δh_o have been calculated from the temperature coefficients of vapor pressure recorded above (Tables I and III) and are given in Table V.

The heats of dilution are based on very small differences in $\Delta p_o/p_o°$, and thus show large probable errors. In view of the experimental difficulties, the consistency of the data must be considered satisfactory, but it is not possible to say with certainty what is the form of the $\Delta h_o \sim w_r$ curve. Hildebrand[17] and Scatchard[18] have related the heat of mixing of two nonpolar liquids with

the difference between their evaporation energies per cc. (α_1 and α_2). Using a number of simplifying assumptions, they derive an equation which may be written:

$$\left.\begin{aligned}\Delta h_1 &= \frac{1}{\rho_1}(\sqrt{\alpha_1} - \sqrt{\alpha_2})^2 v_2^2 \\ \Delta h_2 &= \frac{1}{\rho_2}(\sqrt{\alpha_1} - \sqrt{\alpha_2})^2 v_1^2\end{aligned}\right\} \tag{16}$$

where ρ and v represent density and volume fraction, respectively. A considerable body of evidence has been brought forward[19] to show that an equation of the form $\Delta h_1 = k_1 v_2^2$ is usually obeyed by binary mixtures of nonpolar liquids. For a mixture of rubber and benzene, the volume fraction is almost identical with the weight fraction, so that we might expect the heat of dilution to be given by $\Delta h_o = k_o w_r^2$. This equation describes the results in dilute solutions if we put $k_o = 0.7$ cal. per g., but at higher concentrations Δh_o is much larger than $0.7 w_r^2$, and varies more rapidly than w_r^2.

Another approach to the problem has been made by Langmuir[20], who relates the heat of evaporation of a liquid with the energy of the increased molecular surface. The heat of dilution of one liquid by a second is thus derived as a function of the molecular surface fractions A_1, A_2 of the components instead of the volume fractions. If a_1, a_2 are the molecular surface areas per g. of the two liquids, Langmuir's result is:

$$\begin{aligned}\Delta h_1 &= a_1 \phi A_2^2 \\ \Delta h_2 &= a_2 \phi A_1^2\end{aligned} \tag{17}$$

where ϕ is a function of the surface energies of the liquids, but not of the composition of the mixture. Despite difficulties in interpreting the surface area of a molecule Smyth and Engel[21], found this treatment to give a satisfactory interpretation of the partial vapor pressures of a number of binary mixtures, and to fail badly only when one of the components was highly polar (water or alcohol). The surface fractions are related to the weight fractions by the expression:

$$\frac{A_1}{A_2} = \frac{a_1 w_1}{a_2 w_2} \tag{18}$$

Replacing subscripts $_1$ and $_2$ by $_o$ and $_r$, and eliminating A_r from (17) and (18), remembering that $A_o + A_r = 1$, we obtain for the heat of dilution:

$$\Delta h_o = a_o \phi \left\{ \frac{w_r}{\frac{a_o}{a_r} - \left(\frac{a_o}{a_r} - 1\right) w_r} \right\}^2 \tag{19}$$

This equation has been employed to represent our heat data by putting $a_o\phi = 4.5$ cal. per g.; $a_o/a_r = 2.53$. The comparisons given in Table V show the fit to be satisfactory. The value of a_o/a_r to be expected from molecular considerations is a little difficult to assess, but the above figure seems not unreasonable. If, following the usual practice, both molecules are treated as spheres, $a_o/a_r \backsimeq 15$. It is obvious that the surface area of the rubber has here been grossly underestimated, and it will be more nearly accurate to compare the surface areas of benzene and a short-chain aliphatic hydrocarbon, which gives

$a_o/a_r \backsimeq 1$. It may be noted that, with $a_o/a_r = 1$, the equation reduces to the same form as (16), so that the two methods of approach are not mutually exclusive.

For the purposes of interpolation we have therefore employed the following expressions for the heats of dilution and solution:

$$\Delta h_o = 4.5 \left(\frac{w_r}{2.53 - 1.53 w_r} \right)^2$$
$$\Delta h_r = 1.78 \left(\frac{2.53 w_o}{1 + 1.53 w_o} \right)^2 \qquad (20)$$

These equations give for the heats absorbed on adding (1) 1 gram of benzene to excess rubber, (2) 1 gram of rubber to excess benzene, values of 4.5 and 1.8 calories, respectively, figures which are closely similar to those found for mixtures of benzene with simple hydrocarbons[22]. This result indicates that the difference in the heats of solution per gram between a high molecular and a low molecular hydrocarbon is small, from which it is justifiable to assume that the effect of molecular weight on the heat of solution of rubbers of different molecular weight will be negligible. This assumption has already been made in combining the heat data for the three different rubbers in Table V.

Entropy of Dilution and Solution

The entropy of dilution was calculated from the free energies based on Figure 12, and the values of Δh_o obtained from Equation (20). In Table VI,

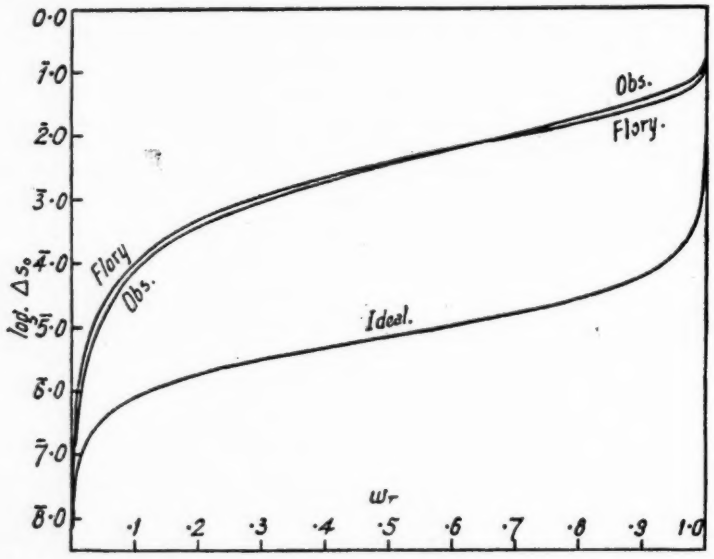


Fig. 13.—Calculated and observed entropies of dilution. Intermediate fraction.

a comparison is made between Δg_o, Δh_o and $T\Delta s_o$ for the intermediate fraction. Figure 13 compares the observed Δs_o with its ideal value ($-R \ln N_o$) and with the values calculated from Flory's theory (see below) by putting $M_e = 100$.

The very large discrepancy between the experimental and "ideal" entropies appears to be a general property of large molecules, and has been discussed recently by a number of authors[23]. In the simplest possible terms, the discrepancy has been taken to mean that, except in highly dilute solutions, the rubber molecules are not the effective units in determining the thermodynamic behavior of the system. The conception of a rubber molecule which behaves as though segmented has been elaborated by Powell, Clark and Eyring[24], and especially by Meyer[25]. A statistical treatment of Meyer's model, carried out by Flory[26], leads to the equation:

$$\Delta s_o = -\frac{R}{\beta M_o}\left\{\ln v_o + v_r\left(1 - \frac{1}{x}\right)\right\} \tag{21}$$

where v_o and v_r are the volume fractions of the solvent and rubber, β is the number of solvent molecules which can be replaced by one "element" of the rubber (an element being the effective unit of the rubber), and x is the number of elements in the rubber molecule. If we denote the "molecular weight" of an element by M_e, and neglect the small density difference between rubber and benzene, Equation (21) may be written:

$$\Delta s_o = \frac{R}{M_e}\left\{\ln\frac{1}{w_r} - w_r\left(1 - \frac{M_e}{M_r}\right)\right\} \tag{22}$$

In this equation, M_e is the only adjustable parameter, and, since $M_e \ll M_r$, the entropies obtained will be inversely proportional to the value assigned to M_e. The curve given in Figure 13 was derived by assuming $M_e = 100$, and will be seen to give approximately the correct entropy over the whole range of composition. The failure of (22) to fit accurately can be represented formally by using the equation to calculate M_e, which is now treated as a function of w_r. For sufficiently small w_o, $\Delta s_o __ -\frac{\Delta g_o}{T} = \frac{R}{M_o}\ln\frac{p_o^o}{p_o^m}$. Experimentally we find in this region $p_o^m/p_o^o = \alpha w_o$, so that $\Delta s_o \to \frac{R}{M_o}\ln\frac{1}{w_o}$ and (comparing with Equation (22)) $M_e \to M_o$. For small w_r, Equation (22) reduces, on expanding the logarithm to the 2nd power of w_r, to:

$$\Delta s_o \backsimeq \frac{R}{M_r} w_r + \frac{R}{2M_e} w_r^2 \tag{23}$$

Using the observed Δs_o to calculate M_e at $w_r = 0.01$ gives the following values:

Intermediate fraction	$M_r = 28 \times 10^4$,	$M_e = 290$
55/45 fraction	15×10^4,	300
Degraded rubber B	8.5×10^4,	305
Degraded rubber A	3.8×10^4,	340

Since a variation of M_e by a factor of only 4 covers the whole range from $w_r = 0$ to 1, Flory's equation must be accounted a notable advance in the theory of high polymer solutions. A disturbing feature is the failure of the theory to give an accurate description of the properties of dilute solutions. In Figure 14, we plot $\frac{\Delta s_o}{w_r}$ as a function of w_r for the osmotic pressure region.

According to (23), these plots for the four rubbers should be linear and parallel. As drawn they fulfil neither requirement, and although any one of them could be straightened by changing the values of Δh_o (without exceeding the experimental error), they cannot all be made linear and parallel without the unlikely assumption that the heats of dilution are different for the four rubbers. Other

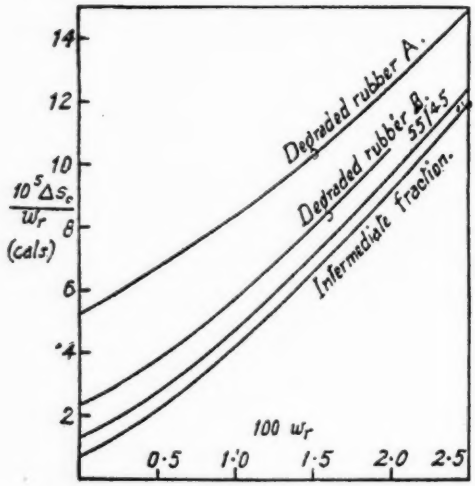


FIG. 14.—Entropy of dilution for various rubbers in the osmotic region.

recent attempts[27] to treat the thermodynamics of polymer solutions also lead to an equation of the same form as (23), and it has been widely stated[28] that such a law holds. The present work is probably the first of sufficient accuracy to test the law and, though not entirely conclusive, certainly suggests that the law is only approximately valid. In terms of Flory's treatment, the deviations are expressed in a significant change of M_e in this region of dilute solutions.

Table VI shows Δh_o and Δh_r to be of the same order as $T\Delta s_o$ and $T\Delta s_r$, respectively, except for small values of w_o or w_r. The ratios $\Delta h_o/T\Delta s_o$ and $\Delta h_r/T\Delta s_r$ lie, respectively, between 0.55 and 0.25, 0.3 and 0.1 over the main part of the concentration range and, except for small w_r, are independent of the molecular weight of the rubber. This last observation is entirely contradictory to the assumption underlying the work of Brønsted[29] and Schulz[30] on the solubility of high polymers. Taking the molar entropy of solution to have its ideal value (almost independent of the molecular weight of the polymer), the distribution of the polymer between two phases is written $c_1/c_2 = e^{-\lambda/RT}$ where λ is the molar heat of transference from phase 2 to phase 1. Taking our measured value for Δh_r as 1.8 calories for the complete solution of 1 gram of rubber, the molar heat of solution of the intermediate fraction is 5×10^5 calories. According to the above theory, this gives $c_1/c_2 \backsimeq e^{-1000}$, so that rubber should be completely insoluble in benzene. Actually, the main factor governing the solution of rubber in benzene is the abnormally large entropy of solution, which is completely neglected in the theories of Brønsted and Schulz.

Table VI gives the impression that $-\Delta g_r$ and Δs_r are finite at $w_o = 1$, whereas it is evident from the general properties of binary mixtures that they should become infinite. The discrepancy is only an apparent one, since, for

$w_r < 10^{-4}$, we can write $T\Delta s_r = 6.20 - 2.1 \times 10^{-3} \ln w_r$, in which the second term, though ultimately tending to infinity, becomes important only in solutions in which the concentration of rubber is so small that the effect of the solute cannot be detected experimentally.

SUMMARY

Equations are developed relating the thermodynamic properties of a mixture of rubber + liquid with the vapor pressure of the liquid above the mixture.

Experimental methods are described for the determination of vapor pressure over the whole range of composition of the mixture. By the use of four different methods, it was possible to measure relative vapor pressure lowerings $\Delta p_o/p_o°$ from 2×10^{-6} to 0.997.

Complete vapor pressure data are given for rubber-benzene mixtures at 25° C, together with the calculated Gibbs' free energies of dilution and solution. Temperature coefficient measurements at a number of concentrations are employed to calculate heats of dilution, and these are interpolated by a modified form of an equation due to Langmuir. In this way the heats of dilution and solution are also obtained over the whole range of composition. Combining the heat and free energy data gives the entropies of dilution and solution.

The entropy of dilution is approximately twice the heat of dilution over a wide concentration range and, except in dilute solutions (< 5% rubber), both are independent of the molecular weight of the rubber. The entropy of dilution is very much larger than its ideal value, and can be approximately represented by an equation of Flory, though there are significant discrepancies in the region of dilute solutions.

The molar heat of solution of rubber is so large that the miscibility of rubber and benzene can be explained only by the anomalously large entropy of solution.

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CHEMICAL REACTIONS OF RUBBER *

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Most of the literature descriptive of the various known derivatives of rubber is found published as patents rather than as technical papers, thus indicating the commercial possibilities that may be expected from these developments. Fisher[1], Schidrowitz[2] and, more recently, Jones[3] have summarized and discussed the chemistry of rubber and its commercial derivatives.

The decomposition of rubber by heat has been studied by several investigators. Williams[4] showed that isoprene is one of the main products formed by the destructive distillation of either caoutchouc or gutta percha. Later investigators have shown that slow heating *in vacuo* at 300° C converts somewhat more than one-half of rubber hydrocarbon into a solid, thermoplastic, isomeric product, which has a high molecular weight and less unsaturation than that of the original hydrocarbon[5]. Rapid heating, especially *in vacuo*, converts almost all the rubber into volatile products. The most complete investigation of the products obtained by the heat decomposition of rubber apparently was carried out by Midgley and Henne[6]. These investigators destructively distilled 200 pounds of pale crepe rubber in 16-pound batches by raising the temperature as rapidly as possible to 700° C at atmospheric pressure in an iron kettle. The condensate was fractionally distilled, and cuts were made every degree between 50 to 176° C. Each cut was then separately examined. Twenty-three different hydrocarbons were identified in the distillate.

On the other hand, rubber mixed with 10 per cent by weight of aluminum chloride, and decomposed by heat, produces no isoprene, and yields products entirely different from those formed by destructive distillation. From 200 grams of rubber so treated, there were produced 14 liters of gaseous products and 140 grams of liquid products[7]. In a later paper, by heating rubber for from 1.5 to 2 hours at 400° C, under a pressure of 150 atmospheres of hydrogen in the presence of molybdenum sulfide or nickel deposited on aluminum oxide, only a mobile liquid product results, which consists of saturated and unsaturated hydrocarbons[8].

A number of products have been obtained by the oxidation of latex or of dry rubber, some of which are available on the market. A sticky latex, claimed to have certain advantages as an adhesive over ordinary latex, has been prepared by oxidation with hydrogen peroxide[9]. By oxidation of rubber with peracetic acid[10], products are obtained which are claimed to be adaptable for use in films, lacquers, and mouldings, but thus far none of these has apparently been produced from such a material.

When rubber is treated with oxygen in the presence of certain catalysts, such as cobalt linoleate and other paint driers, disaggregation and oxidation take place, and a series of products are obtained which vary in oxygen content from a small fraction of a molecule of oxygen up to 0.5-molecule for each C_5H_8 unit. The product can be made by milling the catalyst into rubber, or by aerating at 80° C a rubber solution containing the catalyst[11]. Depending on

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the degree of oxidation, the products formed vary from alcohol- or acetone-soluble to insoluble products. The soluble products are used in paints and varnishes; and since they are thermosetting, they are used for the impregnation of insulating coils, which are finished by baking.

An oxidized rubber product is obtained by treating unmasticated rubber in a solvent with oxygen or with a substance liberating oxygen, such as hydrogen peroxide and perborates in the presence of a metallic oxidizing catalyst[12].

According to another United States patent[13], a solution of acetyl peroxide in benzene is mixed with a benzene solution of rubber and, after the mixture has stood for 24 hours, it is steam-distilled, dried, and extracted with ether. A hard yellow thermoplastic is obtained, which can be plasticized with aryl phosphates and alkyl phthalates.

Although no commercial developments followed from the work, the general structure of rubber hydrocarbon, together with the position of the double bond in a unit group, was determined almost entirely by ozonolysis through the studies of Harries. Ozone adds to an olefin at the double bond, forming an ozonide which, on hydrolysis, is decomposed into an aldehyde or ketone, according to the groups attached to the double-bonded carbons. By this general procedure Harries found that the decomposition products consist of levulinic aldehyde, levulinic acid, and levulinic acid peroxide, with smaller proportions of formic acid and of succinic acid[14].

Rubber is an unsaturated hydrocarbon and, in view of this, is a substance capable of hydrogenation. Pummerer and Burkard[15] obtained a partially hydrogenated product by reducing a solution of purified rubber in hexane and in methyl cyclohexane, using platinum black as a catalyst. The product was elastic and similar to rubber in many respects, but was colorless. Working under different conditions, Staudinger and Fritschi[16] hydrogenated rubber completely at 270° C, under 100 atmospheres' pressure. This product also was colorless, but did not possess any elastic properties. Although several patents have been granted claiming the use of hydrorubber for various objects, it is not known that any of these have actually been employed. A white amorphous product is obtained by the hydrogenation of rubber[17]. Hydrogenation may be carried out in the presence of hydrocarbons[18]. Such products may be used to increase the viscosity of lubricating oil[19].

The reaction of halogens with rubber has been studied for a longer time, and by many more investigators than have the other nonsulfur derivatives of rubber. Although the first work was reported in 1801 by Roxburgh, it is not apparent that he obtained a chlorinated rubber, since he employed carbon disulfide as a solvent, which itself is readily chlorinated. Engelhard and Day[20] exposed lumps of rubber to the action of chlorine, and preferably passed a stream of chlorine through a solution of rubber in chloroform or benzene[21]. Products ranging from a flexible material to a hard leatherlike mass were obtained. Although several other patents were granted on methods of producing chlorinated rubber, the nature of the reaction was not studied for some time. Gladstone and Hibbert[22] extensively investigated this reaction, and found that chlorine reacted with rubber by addition and also by substitution. By the analysis reported for the product, it appears that there were six chlorine atoms added and two chlorine atoms substituted in the parent $C_{10}H_{16}$ group, with the final product having the formula $C_{10}H_{14}Cl_8$. It is questionable if the analysis was correct, since later work has shown the heptachloride, $(C_{10}H_{13}\text{-}Cl_7)x$ to be the product.

The first commercial development of a chlorinated rubber product is evidently due to Peachey[23] in England. According to these patents, rubber heptachloride, $C_{10}H_{13}$-Cl_7, is produced by passing chlorine in excess into a chloroform or carbon tetrachloride solution of rubber. Lesser quantities of chlorine yield a more flexible and softer product. This material was marketed under the name of Duroprene, and was suggested for use in a varnish for acidproofing and waterproofing paper, leather, and fabrics.

Later, chlorinated rubber attracted more attention, and several investigators, particularly the Germans, developed methods of producing chlorinated rubbers which form solutions of lower viscosity, thereby increasing the field of application. It was found that the nature of the product depended on the temperature of chlorination, the nature of the solvent employed, and the degree to which the rubber was broken down[24]. Chlorinated rubbers vary with respect to resistance to heat, viscosity of solutions, and film-forming capacity. The commercial products are quite nonflammable and are resistant to petroleum solvents and to oxidizing acids, but are soluble in coal-tar solvents. The main application of the product appears to be as corrosion-resisting paints and lacquers. Solid chlorinated rubber products having a cellular structure are described by Montgomery[25] as obtained by heating in a mould an aqueous emulsion or dispersion of a solution of chlorinated rubber in a volatile solvent. An expanded fibrous product is obtained by Schidrowitz and Redfarn[26] by heating solid chlorinated rubber under pressure and releasing the pressure while maintaining the temperature. The product has a specific gravity of but 0.087, and possesses a cellular structure.

The hypochlorite of rubber is obtained by shaking a benzene rubber solution with ethyl hypochlorite and removing the solvent[27]. The dried product is stated to be resistant to solvents.

A yellow resin results from reacting under reflux a benzene solution of rubber with phenyl sulfur chloride[28].

Other halogen derivatives of rubber have been prepared, but apparently have not been developed commercially, probably because of their cost. Rubber is converted into soft tacky or hard brittle thermoplastic products by treating a carbon tetrachloride solution of rubber with boron trifluoride in acetic acid[29]. Rubber hydrofluoride, a leatherlike or hornlike product, is obtained by reacting rubber in a solvent with hydrofluoric acid[30]. A similar product, usable as a lacquer or an adhesive, results from milling aqueous hydrofluoric acid into rubber, and heating the mix in an autoclave for 16 hours at 100° C[31]. A product resembling gutta-percha, which can be obtained as a hard porous material, results from mixing rubber with up to 10 per cent by weight of phenyldiazonium fluoborate, and heating for two hours in an oven at 130–140° C[32].

A rubber fluoride, $C_5H_8F_2$, containing up to 30 per cent of fluorine, is made by treating rubber in carbon tetrachloride solution with fluorine mixed with 10–50 per cent by volume of an inert gas, such as nitrogen, air, or carbon dioxide[33].

A solution of rubber containing a dehydrating agent is treated with a fluorine compound, such as boron or phosphorous halides. The products vary in properties, depending on the length of treatment. The products are thermoplastic, but brittle[34]. Variations in the production of rubber fluorides, or products resulting from the action of fluorine compounds on rubber, are described in three patents[35].

An interesting development is covered by British patent No. 523,734 to Dunlop. By treating a solution of rubber in carbon tetrachloride, containing paraformaldehyde with gaseous boron trifluoride, a gel is obtained. After removal of the solvent, a hard white rubber derivative remains; this can be sheeted out on a mill only with difficulty. By treating vulcanized rubber similarly, a surface coating is formed that is said to make the rubber more resistant to surface abrasion and less easily deformable.

Bromine acts in a manner similar to chloride, and reacts by substitution as well as by addition. The tetrabromide, $C_{10}H_{16}Br_4$, is a white amorphous solid, soluble in very few solvents[36].

Iodine forms various unstable products with rubber of no definite composition and sometimes containing oxygen in addition to iodine[37]. A later investigator[38] reported that a white powder soluble only in chloroform and alcohol, but decomposed by heat, was obtained by exposing to sunlight a mixture of a 1 per cent solution of rubber in chloroform with iodine. Neither the iodide nor bromide of rubber has apparently been put to industrial use.

Rubber dibromide reacts with triphenyl phosphine and triethyl phosphine as they do with ordinary alkyl halides[39]. The reaction is not complete, and the products behave like saturated compounds which are insoluble in benzol and chloroform. The solid forms are elastic. Rubber tetrabromide and molten phenol, in the presence of aluminum chloride and preferably ferric chloride, evolve hydrobromic acid and form a product tetroxyphenylpolyprene, $C_{10}H_{16}(O \cdot C_6H_4)_4$[40]. The products possess high molecular weights, are colored, and are soluble in toluene.

A class of rubber derivatives or reaction products, varying in physical characteristics from soft rubbery types through the gutta-percha and balata types to hard, shellaclike types, all consist of a hydrocarbon of the formula $(C_5H_8)x$, and have less unsaturation than rubber itself. The unsaturation varies from about 57 to about 20 per cent that of rubber. Since the change in unsaturation is thought to be due to internal cyclic arrangement, the products are known as cyclic rubbers. The products have been described by Staudinger[41] as monocyclorubbers and polycyclorubbers, depending on whether the unsaturation was half or less than half that of rubber.

Monocyclorubber is a white, nonelastic powder that sinters at 120° C, and melts at about 130° C. It is soluble in benzene and petroleum ether and insoluble in alcohol and ethyl ether. Polycyclorubbers are asbestoslike masses, lacking all elastic properties. They are soluble in benzene, chloroform, and carbon disulfide, and insoluble in alcohol and acetone. The physical properties vary with the conditions of preparation.

These cyclorubbers are usually produced by the action of acids combined with heat on rubber. In 1910, Harries showed that an amorphous powder, insoluble in the usual rubber solvents and more saturated than rubber, resulted from the action of sulfuric acid on Para rubber at ordinary temperatures. The development of the products of this class of commercial importance was due to Kirchhof[42] and Fisher[43]. There are a number of patents in several countries on the manufacture and application of such cyclorubbers.

In Fisher's work, sulfuric acid was first employed as the cyclicizing agent[44], followed by a study of *p*-toluene sulfonyl chloride and various sulfonic acids[45]. The method followed is to mill the reagent into rubber on the ordinary mixing mill, and heat the resulting mix. It was found that, according to the activity and quantity of the particular cyclicizing agent, the concentration, and temperature employed, the properties of the product obtained could be varied

widely. Mild cyclicization produces products which resemble gutta-percha and balata; more vigorous treatment produces substances of a hard, balatalike nature and finally shellaclike materials. These various products have been given the name of "thermoprenes" (signifying a thermoplastic unsaturated hydrocarbon derived from polyprene) with letters GP (resembling gutta-percha), HB (like hard balata) and SL (meaning shellaclike). Thermoprenes vulcanize on heating with sulfur, and combine with up to 21 per cent sulfur. They dissolve with difficulty in rubber solvents. They react with halogens, halogen acids, and oxygen. The most important property of thermoprenes is that of producing adhesion of vulcanized rubber to metals, wood, and like surfaces. This process is widely used for the lining of tank cars, storage tanks, and the like with chemical-resistant rubber, and it produces an effective and firm union for use at ordinary temperatures. The adhesive joint softens at about 60° C.

Various other thermoplastic derivatives of rubber have been described, mainly in the patent literature, which differ in the cyclicizing agent employed. Thus a product more heat-plastic than rubber and of lower unsaturation, is obtained by mixing anhydrous salts such as iodides of aluminum, antimony, iron, and other amphoteric metals with rubber, and heating at 200 to 250° C[46]. A thermoplastic product results from treating rubber with a mixture of a halide salt and a soluble salt containing water of crystallization. In an example, rubber is milled with alum and phosphorus pentachloride, followed by heating from 5–15 hours at 160° C[47]. Fisher also has shown[48] the production of cyclorubbers by the milling together into rubber, and heating of a phenolic substance, such as phenol, pyrocatechol and naphthol, with an acid or a compound capable of producing an acid on decomposition by heat.

Several variations in procedure have been described for the phenolic-rubber products. According to one method[49] rubber is treated on a mill with 10 per cent by weight of β-naphthol and 4 per cent by weight of sulfuric acid. After the reaction is over, as indicated by a drop in temperature, approximately 2 per cent of paraformaldehyde is added, and the milling continued. At the end of 30 minutes' total milling, the batch is sheeted off the mill as a dark brown thermoplastic, which softens at 90° C. This product is called Isolac[50]. A somewhat similar product is made by heating rubber with a phenol in the presence of an acid at 170–180° C. The feature of this patent[51] is the use of an acid, such as hydrochloric acid, which does not combine with the phenol. In another process[52], the reactants are all brought together simultaneously in the presence of a solvent. The product, a white powder, is said to be capable of being moulded at 140–160° C.

Sebrell, Bruson and Calvert[53] obtained thermoplastic products by reacting a benzene solution of purified rubber with various anhydrous metallic halides, such as stannic chloride, and ferric chloride, to form molecular addition compounds which, on treatment with alcohol, liberate metallic chlorides and form cyclorubber.

Acids such as chloro- and bromostannous acids form thermoplastic rubbers when mixtures of the acid and rubber are heated. The products formed vary from tough products resembling balata to hard, ebonitelike substances[54]. The product Plioform is a resin described by Thies and Clifford[55]. These products, which are thermoplastic and are resistant to many acids and alkalis and to solvents of the acetone type, are marketed as moulding powders and also in the form of rods and tubes.

Other types of cyclorubbers have been patented. According to British patent 486,878, leatherlike products result from vulcanizing a material obtained by heating with an aldehyde an acidic aqueous dispersion of rubber containing a protective colloid. A chloroform solution of rubber treated for two days at 15° C with peracetic acid prepared from acetic anhydride and hydrogen peroxide, after being freed from reactants by washing and steaming, forms a plastic product containing 20–23 per cent of oxygen[56]. Instead of using the preformed per acids, they may be formed *in situ*. Thus a chloroform solution of rubber is treated with glacial acetic, formic, or chloroacetic acids, and hydrogen peroxide added. After refluxing the mixture for 16–18 hours at 65° C, a yellow resin results[57]. A solution of rubber treated with the fraction obtained by distilling a mixture of phosphorous pentachloride or phosphorous oxychloride and phosphoric acid becomes less viscous, is colored reddish brown, and yields a plastic product[58].

Several alternative methods of reacting rubber with phosphorous halides have been described. Thus a chlorobenzene solution of rubber, treated with a mixture of phosphorous tri- and pentachlorides and heated at 90–95° C for three to eight hours becomes low in viscosity in a highly concentrated solution[59]. A thermoplastic product, softening at 100–110° C, is obtained when a benzene solution of rubber is treated with 7–10 per cent by weight of phosphorous oxychloride at 40° C[60]. A tough, hard thermoplastic product is formed by agitating a solution of rubber for two hours, followed by 10 hours' standing, both at room temperature with phosphorous oxychloride, to which is added 0.1 its weight of water and air-blown[61]. A modification of this last process involves the use of ultraviolet radiation to accelerate the reaction[62]. Other modifications of the action of phosphorous oxyhalides on rubber are described[63].

It seemed of interest to study further the action of phosphorous halides on rubber. In one experiment, 100 grams of phosphorous pentachloride was added to 2,000 grams of a 5 per cent benzine solution of rubber, and the mixture allowed to stand 48 hours. The benzene was then removed, and the product washed and dried. There was approximately a 30 per cent increase in weight resulting from the reaction. The product was rubbery in nature, but failed to cure by using conventional methods. The only method found for handling the product was to mill in approximately 30 per cent of zinc oxide and cure 30 minutes at 134° C. The stock cured to a hardness of 70, and the product, of poor tear-resistance, was much more resistant to kerosene than is rubber. The rubber-phosphorous pentachloride product has been found to react further with aromatic hydrocarbons, for example, with a substituted phenanthrene, to form a rather soft, tough rubberlike product which, compounded with 25 per cent zinc oxide, 40 per cent carbon black, 3 per cent sulfur, 1.25 per cent accelerator, 3 per cent stearic acid, 2 per cent pine tar, and 1.5 per cent antioxidant, cured to a hardness of 120 and had 1,135 pounds per square inch tensile strength at 60 per cent elongation. The stock swelled in kerosene only 5 per cent, compared with 45 per cent for a rubber stock. The stock showed no decrease in tensile strength after aging 120 hours at 70° C, under 300 lbs. per sq. in. oxygen pressure. The stock showed about the same resistance to ozone as rubber, and was worse than rubber in abrasion index, and higher than rubber in permanent set. After immersion for eight days at room temperature, it was much superior to rubber and to certain synthetics in its resistance to petroleum and benzene hydrocarbons, chlorinated solvents, ether, and acetone, but was slightly worse than rubber in water. Immersion in solvents for

four days at 70° C resulted in a loss in weight in all solvents with the exception of water. Extraction was greatest (24%) in the case of gasoline.

Another type of cyclorubber is obtained when a benzene solution of rubber is treated on the steam bath with trichloroacetic acid[64] or with dimethyl sulfate[65]. A carbon disulfide or benzene rubber cement, treated with phthalyl chloride or phosgene and aluminum chloride or with zinc chloride in acetic anhydride, or alcohol, yields tough products insoluble in rubber solvents, which are capable of vulcanization[66]

Cyclorubbers produced by the action of heat alone are capable of hydrogenation. Staudinger[67] saturates such a cyclorubber with hydrogen under 50–80 atmospheres' pressure, in the presence of platinum or nickel as a catalyst, by heating 20 to 30 hours at 270° C. Hydrocyclorubber is a white amorphous solid, which is soluble in benzene, chloroform, and ether, and is stated to be usable as a substitute for gutta-percha. Various methods of producing cyclicized rubber are described by Stevens and Miller[68].

An acid derivative of rubber which is not a cyclorubber is the addition product with a halogen acid. For example, if hydrogen chloride gas is passed into a benzene solution of rubber at ordinary temperature, a compound results which can be easily separated by steam distillation and washing. From such a product the manufacture of transparent films and sheets has been developed[69]. The main claims for the commercial hydrochloride, marketed under the trade name of Pliofilm, in connection with its use for wrapping and packing, are that it is strong, stretchable, tear-resistant, moistureproof, and not affected by oil or grease. It is readily heat-sealed by heating at 105–130° C. For photographic films, it is stabilized by admixture with an anti-acid substance, such as pine oil.

Another type of a modified rubber hydrochloride composition is that obtained by milling and moulding the hydrochloride with up to 10% its weight of various metallic phosphates[70]. Light colored stiff products are obtained. Rubber hydrochloride in toluene solution has been reacted with a metallic sulfide or polysulfide to form a product that can be moulded[71].

Rubber hydrochloride can be dehalogenated by heating with pyridine or piperidine, preferably in a solvent at 125–145° C, to produce a halogen-free product different in properties from the hydrochloride and also from rubber itself[72]. Alternatively, the rubber hydrochloride dissolved in chloroform is mixed with zinc dust and mineral acid and heated. The halogen-free product is dried[73].

Concentrated nitric acid reacts slowly with crude rubber in the cold, but on warming or by the use of fuming nitric acid, the reaction becomes violent. A solution is finally obtained, which on pouring into water, forms a flocculent yellow precipitate[74], which closely approximates the formula $C_{10}H_{12}N_2O_6$. A product said to be suitable for impregnating, coating, and insulating purposes is formed by treating a carbon tetrachloride solution of rubber with concentrated nitric acid[75]. This product has the formula $(C_5H_7NO_2)x$, and slowly decomposes at room temperature. Rubber can be depolymerized by treatment with 36° Be nitric acid[76].

Since the reaction of nitric acid and hydrogen chloride with rubber had both been described, it was thought interesting to try the effect of a mixture of these two acids, as aqua regia. No reference was found reporting such work. Accordingly, a 20 per cent benzene solution of pale crepe rubber was treated with aqua regia at room temperature, with rapid stirring, until the mixture became too stiff to stir. The reacting mass was allowed to stand overnight

and was then extracted repeatedly with boiling water until the wash-water reacted neutral to Congo red. The products were then dried overnight in an oven at 70° C. Using one part by weight on one part of pale crepe rubber, the product was dark brown and spongy, with no elastic properties. This product was found to contain 7.4 per cent chlorine and 2.8 per cent nitrogen. A second sample, reacted as described in the ratio of one part of pale crepe rubber to 2.5 parts of aqua regia, formed a light-brown brittle product, containing 9.9 per cent chlorine and 6.8 per cent nitrogen. A third cement of pale crepe rubber, reacted in the ratio of one part rubber to five parts aqua regia, also formed a hard light-brown brittle product, containing 24.1 per cent chlorine and 7.1 per cent nitrogen. All three products were only very slightly soluble in 100 times their weight of benzene or acetone. None possessed thermoplastic properties, nor could they be plasticized by the use of equal parts by weight of any of the commonly used plasticizers. Furthermore, the products decompose on heating to about 70° C.

A true sulfonate of rubber is obtained by adding an ether solution of rubber to an ether solution of chlorosulfonic acid, keeping the mixture cold. The sulfonation is continued with agitation for 24 hours at 20° C[77]. A water soluble sulfonic acid derivative is obtained by treating rubber with oleum or with chlorosulfonic acid[78]. A balata or gutta-percha substitute is obtained by treating rubber with *p*-toluene sulfonic acid[79]. In another patent[80] the distillate having a boiling range up to 350° C, obtained by heating rubber, is treated simultaneously with butyl alcohol and 93 per cent sulfuric acid, with agitation at 40–45° C. After treating with lime to form a calcium sulfonate, filtering, transposing with dilute sulfuric acid, and neutralizing with sodium carbonate, a white waxy solid is formed. The products are soluble in water, ethyl acetate, and acetone, and insoluble in benzene and chlorinated hydrocarbons.

When passed through a benzene solution of rubber, nitrogen peroxide forms a granular precipitate, which, after solution in acetone and precipitation by ether, produces a buff-colored powder[81].

Nitrogen trioxide and nitrogen tetroxide both form addition products with rubber-yielding powders, one of which, Nitrosite C, has been adapted to the quantitative determination of the rubber hydrocarbon in crude and vulcanized rubbers[82].

Certain nitroso compounds also form addition products with rubber, such as nitrosobenzene[83] and the nitroso toluenes, and ethers of nitrosophenols[84]. By mixing rubber with nitrosoamines and heating at 80° C for 30 minutes, tacky products are obtained[85]. A similar tacky product is formed with nitroso β-naphthol[86].

Chromyl chloride forms addition products with the terpenes, and forms a like compound with rubber[87]. The product is a brown powder, insoluble in most organic solvents, and decomposed by water with formation of resinous products.

Rubber, as a hydrocarbon, has been reacted by the well known Friedel-Crafts reaction with aromatic halogen derivatives, particularly benzyl chloride[88]. By the method described, anhydrous aluminum chloride in carbon tetrachloride is poured quickly into a cooled carbon tetrachloride solution of rubber containing benzyl chloride. Hydrogen chloride is evolved, and a gray-white spongy mass is formed, which remains as a white amorphous product. The mixture is warmed on a water bath until no more acid is evolved; the solvent is removed, and the product washed with acetone and dried. The

nature of the product varies, depending on the reaction conditions. The products are described as readily powdered, as having a density of about 1.10, and as being inert to most organic solvents. They are but slightly thermoplastic. Since benzyl chloride itself polymerizes under the influence of aluminum chloride[89], and since rubber is cyclicized by metallic chlorides[90], there is some doubt regarding the nature of the product described by Kirchhof[91]. In some unreported experiments in which benzyl chloride has been used in ratios between $\frac{1}{64}$ and two mols per mol of rubber (as C_5H_8), both with and without solvents, at temperatures from room temperature to 100° C, with catalyst ratios from 1.8 to 22 per cent by weight on the rubber, and employing the anhydrous chlorides of aluminum, zinc, iron, and tin as catalysts, no single rubber derivative resulted. The products apparently were a mixture of four different products, namely, cyclized rubber, benzyl chloride-rubber derivative, benzyl chloride polymer, and rubber hydrochloride. Increasing the benzyl chloride ratio naturally increases the proportion of the two last products. The low benzyl chloride products are rubbery; those with higher proportions of benzyl chloride resemble leather. The materials are all slightly thermoplastic, but are not thermosetting. Solvents apparently favor the formation of the benzyl chloride polymer. The various products do not appear to possess any favorable properties. Benzyl chloride polymerized by itself yields a brittle product that can be plasticized, but the plasticized polymer does not improve a rubber compound, and although the polymer is insoluble in kerosene and benzene, the rubber stocks containing the polymer are still oil-soluble. The rubber-benzyl chloride polymerized product can also be plasticized, but again the plasticized product does not yield a satisfactory vulcanized product, as the modulus and tensile values are very low.

An interesting series of products recently has been described[92] as obtained from rubber by reaction with maleic anhydride. In the presence of small proportions of benzoyl peroxide, maleic anhydride reacts with rubber in solution by addition at the double bonds. Benzoyl peroxide is necessary for the reaction, but appears to act only as a catalyst. A plurality of products has been obtained, containing from a few per cent up to as much as 120 per cent of maleic anhydride, calculated on the rubber. The various products differ considerably from rubber in physical properties, from tough, somewhat rubbery products through fibrous products to hard brittle products as the maleic anhydride content increases; at the same time the products become less readily soluble in rubber solvents and more soluble in solvents for maleic anhydride. The product further varies in properties with changes in the conditions. The products have not become of commercial importance, although they are of much technical interest because of the variety of products obtainable and the possibility of forming further derivatives through reaction with active groups present. Typical of such products is the resinous product obtained by treating rubber and a phenol at elevated temperatures, followed by reaction with an aldehyde[93].

A rubber conversion product, which in a compounded stock is claimed to show increased resistance to abrasion, is obtained by treating a benzene solution of rubber with such compounds as phthalyl chloride, phosgene in the presence of aluminum chloride, or titanium tetrachloride at room or higher temperatures[94].

Another conversion product, stated as capable of addition to crude rubber for improvement in its properties, results from the treatment of latex or a rubber dispersion with formaldehyde in the presence of acids under such temperature conditions that no isomerization occurs[95].

A nonelastic rubber derivative is obtained by cutting rubber into small pieces and allowing it to stand for 14 days in a closed container at 25° C, in contact with chloromethyl ether. A tough, spongy product is obtained after steam-distilling and drying the product[96].

A hard plastic mass is stated to be obtained by swelling rubber with twice its weight of a solvent, such as tetrachloroethane, and stirring for about one-half hour with stearic acid, after which aluminum chloride is added and the mixture refluxed for six hours at 140° C. The reaction product is cooled, poured into an ice-hydrochloric acid mixture, steam-distilled to remove solvent, washed free from acid, and dried[97].

Azo dyes are as obtainable by reacting rubber di(hydroxyphenyl), formed by the reaction of rubber bromide and phenol, with a diazotized aromatic amine, *e.g.*, sulfanilic acid[98]. Sulfonation produces water soluble dyes[99].

A rubber derivative possessing antioxidant properties is obtained by heating rubber with an aryl amine or a salt of an amine. Thus, rubber heated with aniline or aniline hydrochloride at 250–280° C, under 50–100 pounds' pressure for eight hours, forms a brownish mass, which, after steam-distillation, is thermoplastic and can be used to bond rubber to steel[100].

Rubber is transformed into a benzene-insoluble product by allowing a benzene rubber cement to stand at room temperature for 20 hours in contact with nickel carbonyl or lead tetraethyl. A tough, black gelled rubber is formed[101].

Thioglycolic acid standing in contact with pale crepe rubber for 16 months at room temperature converts the rubber into a product soluble in normal caustic soda solution. Balata reacts in the same manner as rubber, while gutta-percha is not affected[102].

No great success has thus far been attained with three types of products of rubber with synthetic resins: rubber condensed with reagents used to make synthetic resins, with materials formed by the intimate admixture of synthetic resins and rubber, or by sections of rubber and synthetic resins brought together to form laminated products[103]. Several patents disclose rubber or latex combinations with phenol-aldehyde resins[104].

Several such so-called rubber copolymers have been described. One such product is obtained by mixing deresinated rubber with coumarone or indene and heating the mixture for several hours at 130–160° C. Acrylic acid ester or a soluble phenolaldehyde condensate likewise yields thermoplastic products[105].

Another rubber copolymer results from mixing rubber with a softener and an emulsion of acrylonitrile or ester of acrylic acid, and polymerizing[106]. Rubber has also been copolymerized with a hydrocarbon of the butadiene series[107]. In a more recent study, rubber latex, either normal or concentrated, has been blended with an artificial latex or emulsion of polymerized synthetic resins, including acrylonitrile, methacrylic methyl ester and styrene. The mixed latices are then coagulated by the addition of acid, and the coagulum is washed and dried. The coagulum is said to have a uniform texture, with all evidence pointing to the intimate dispersion of the resin particles among the rubber particles. The presence of the resins has a marked stiffening effect, even when the resin content is low. There is also a marked decrease in breaking strength and an increase in permanent set. Although no evidence was presented, it is suggested that such mixtures should produce a compounded stock of improved solvent resistance and wearing properties[108]. Rubber in a solvent or in latex form has been heated with monomeric styrene and a catalyst[109].

Interesting products have resulted from the heating together under polymerizing conditions of rubber latex with styrene. In this work an emulsion of an oxidizing catalyst and monomeric styrene in water was prepared and added to rubber latex stabilized by means of a suitable wetting agent. Sufficient water was employed in preparing the emulsion to reduce the latex from a 60 to 40 per cent dry rubber content. After agitating at about 60° C for approximately 48 hours, the emulsion was coagulated by the addition of alcohol, which also dissolved any unreacted styrene. The rubbery product was then washed and dried. The properties of the product obtained vary directly with the quantity of styrene combined. Reacting with 40 per cent styrene and compounding the product with 10 per cent zinc oxide, 20 per cent whiting, 40 per cent carbon black, 4 per cent sulphur, 3 per cent stearic acid, 2 per cent pine tar, and 1 per cent accelerator, gave a stock curing to a hardness of 68 and having a tensile strength of 1,620 pounds per square inch at 325 per cent elongation. Higher tensile strengths are obtainable with lower styrene additions.

Rubber has been found to react with aryl polyhalides to produce a new type of product. The reaction is readily carried out by treating a solution of rubber in benzene or carbon disulfide at the boiling point of the solvent in the presence of a catalyst, such as aluminum chloride, for a length of time and with the quantity of polyhalide required to produce the type of product desired. After the reaction is complete, the solvent is removed, and the product washed on a rubber washer and dried. The same product may be formed in the absence of solvent by adding the reactants to masticated rubber on the rubber mill and continuing the milling until the reaction was completed. The properties of the product vary directly with the quantity of reactants and time of treatment. Generally speaking, the higher the ratio of polyhalide, the less rubberlike and harder is the product. The products are thermoplastic, and require sulfur and accelerator for curing. The full possibilities of the softer products obtainable have not yet been fully determined, but the hard products possess interesting properties. Compounding 100 parts of a product, the weight increase of which on the rubber reacted was 40 per cent, with 10 per cent zinc oxide, 60 per cent whiting, 10 per cent titanium dioxide, 3 per cent sulphur, and 1.25 per cent accelerator, and curing for 30 minutes at 141° C, a white product of 98 hardness on the hard rubber gauge was obtained. Adding 1 per cent of rubber colors to the mix, colored hard rubber is readily obtainable. The product was found to possess a higher impact strength than hard rubber. The same reaction also has been found to take place with many synthetic rubbers.

A cement of the compounded reaction product can be used for building up plies of cellulosic materials, such as wood, paper, and cotton cloth, or the cement can be thickened by the addition of sawdust or wood flour, and briquettes cured from it.

An interesting property of all these products is their capacity to react further with aromatic hydrocarbons containing alkyl side-chain substituents. With one such hydrocarbon, as much as 240 per cent weight increase on the rubber may be caused. Naturally with the rubber comprising only about 40 per cent of the weight of the product, and the rubber having been modified by chemical reaction, the elastic properties of the rubber have been impaired, but it has been also greatly improved over rubber in other respects, such as resistance to ozone and to various solvents. The product may be used to replace up to 20 per cent by weight of the synthetics in an oil-resisting stock, with no impairment in physical properties, but with improved handling con-

ditions. In quantities from 20 to 50 per cent by weight of the synthetics, the tensile strength and modulus decrease, but the solvent-resistant properties are not affected, although resistance to aromatic solvents is not improved.

A product of theoretical interest, but apparently of little practical or commercial importance, is so-called inorganic rubber, obtained by reacting phosphorous pentachloride with ammonium chloride in a solvent. The mixture is refluxed for 20 hours at 140–145° C. After removal of the solvent, the phosphonitrilic chloride is distilled, and the distillate polymerized by heating at 250° C. A brown rubbery product results, which, however, is unstable and decomposes in the presence of moisture. Several variations in the procedure[110] failed to improve the product. The only method found for curing the polymer consisted in mixing it with 50 per cent by weight of zinc oxide, and heating for 30 minutes at 141° C in a mould. The product cured to a hardness of 80, but possessed very poor tear-resistance.

The foregoing references are not by any means intended to comprise a complete exposition of all the patents and recorded literature on the subject of rubber derivatives. In some of the more active fields, and particularly in those resulting in commercial exploitation, there exist many articles and patents. For example, there have been issued to one assignee a total of twenty-four United States patents related to cyclized rubber, each one of which has not been discussed in this summary. It is, however, thought that at least one reference has been mentioned for every different type of reaction thus far reported to which rubber or rubber hydrocarbon has been subjected.

The nature of the products obtained have varied widely in physical characteristics and in chemical reactivity. The products described have varied from tacky gums to hard, resinlike plastics. Many products resemble leather in nature and sometimes in appearance. The more profoundly the rubber hydrocarbon molecule is altered, the less elastic and the more resinlike is the resulting product.

It has been shown that rubber is a chemically active material, and reacts like any typical olefin hydrocarbon. Under proper reacting conditions, rubber forms addition products with many substances, such as sulfur, oxygen, ozone, hydrogen, halogens, hydrohalides, dithiocyanogen, dithioglycolic acid, and other compounds. Rubber forms substitution products with many other substances, in fact, the study of rubber as a chemical compound has been seriously investigated only in recent years. Further study may well extend its applications into hitherto unsuspected fields of usefulness and value.

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THEORY OF FILLER REINFORCEMENT IN RUBBER *

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There are many active filler substances capable of improving to a considerable extent the mechanical properties of rubber mixes.

The reinforcing effect of fillers is rather a complex problem and is known to depend, not only on the surface area and size of the particles involved, but also the nature and shape of the particles and the nature of the material in which they are situated.

The influence of the surface forces between the filler and matrix has been discussed from a theoretical point of view, particularly by Hock and his collaborators[1]. However, a closer perusal of the available experimental material reveals that the surface energy cannot be the only important factor in the reinforcing effect. It is clear that a particle of a foreign substance embedded within the bulk of the rubber will, in general, have a different volume from the actual space in the material available for it. If it is held firmly enough by the surface forces, the particle will either compress or expand the surrounding medium, depending on whether its size is larger or smaller than the hole in the matrix available for it. Consequently, this particle will become the center of a more or less symmetrical stress (compressional or tensional) field.

In a discussion of filler reinforcement, the elastic energy generated by the particles must be taken into account. In the following it will be attempted to give a brief discussion of this effect and its relation to the previously treated surface effect of the particles. Although this should not be considered a complete theory, it introduces a new feature into the discussion of this subject, provides a basis for further experiments, and might be helpful in assessing the usefulness of fillers in rubber mixes.

THE CHANGE IN THE FREE ENERGY DUE TO THE FILLER

ΔF, the total increase in the free energy due to the filler, is made up of two parts:

$$\Delta F = F_S + F_E \tag{1}$$

where F_S is the total surface energy of the particles in the rubber mix, and F_E is the total elastic energy set up in the matrix by the filler.

The total surface energy is given by the expression: $F_S = \sigma \sum^{N} f_N$, where $\sum^{N} f_N$ is the total surface between the filler and the matrix material and is the total surface of the N filler particles, and σ is the corresponding surface force (surface tension) between the particles and the rubber mix.

$\sum^{N} f_N$ obviously increases with decreasing particle size. For a given total volume of spherical particles, the ratio of the surface to the volume is inversely proportional to the particle radius r. Spherical particles have the smallest

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surface for a given volume. Therefore the surface effect must be greater with thin platelike particles, which have the greatest surface for a given volume.

It should be possible to get an indication of the surface activity of a given filler by measuring the heat of wetting towards a standard liquid, such as benzene or dioxane.

By comparing the heat of wetting, which can be easily measured in a calorimeter, with the reinforcing properties of the same filler in a given mixture, it should be possible to establish a simple relationship between these two effects.

The heat of wetting is given by: $\sigma' (\sum^{N} f_N)$, where σ' surface tension between the liquid and the filler. Obviously the same total surface area comes into operation in both cases, and σ' increases with increasing σ. In both cases the magnitude of the surface force depends on the amount of unsaturation of the surface of the particles, which manifests itself in a similar way towards the rubber mix and the organic liquid.

It is possible that, at least in the case of carbon black, a suitable method to test the activity of the carbon black can be found in the low temperature conversion of para-hydrogen into ortho-hydrogen. These measurements can be carried out quickly, and may give a direct estimate of the unsaturated valency forces on the surface of the carbon particles.

According to the modern concepts of valency forces, there is a continuous change from the (physical) van der Waals forces to the true valency forces. Consequently in the action of the surface forces of highly active particles, no sharp distinction between physical and chemical effects can be made. It is quite possible that the unsaturated atoms on the surface of the carbon black particles may exert a sort of chemical vulcanizing action on the rubber, although it would be difficult to draw any detailed picture of their action.

THE ELASTIC ENERGY (F_E)

The theoretical treatment of this effect is not so simple as that of the surface effect. Fortunately, the case of impurity-hardening in metals has been treated recently by Mott and Nabarro[2], and the theory can be applied with certain modifications to the present case.

For simplicity, spherical particles will be considered. If r_0 is the radius of the particle, it can be shown that the strain in the matrix is a shear without dilatation. The shear stress at a distance R from the particle is given by $G\epsilon r_0^3/R^3$, where ϵ depends on the material of the particle and of the rubber mix, and equals: $\dfrac{3K\delta}{3K + 4G}$.

The modulus of shear of the rubber material is expressed by: $G = \dfrac{E}{2(1 + \mu)}$, where K is the bulk modulus of the filler substance ($1/K$ = compressibility), E is Youngs' modulus of the matrix, μ, Poisson's ratio of the matrix, and δ is the excess in the linear dimensions of the particle over the linear dimensions of the hole available for it in the matrix. The latter will partly depend on the mechanical process used in the preparation of the rubber material under consideration.

If N particles are present per unit of volume, the average distance of a point in the matrix from the nearest of them is $R_a \sim N^{-\frac{1}{3}}$ and, consequently, the average shear stress in the matrix is given by: $S \backsimeq G\epsilon r_0^3 N$.

If the ratio $\left(\frac{\text{total volume of the filler particles}}{\text{total volume of the rubber mix}}\right)$ be β, then

$$S \sim G\epsilon\beta \tag{2}$$

The shear stress is independent of the size of the particles, and depends only on the quantity of them, as can be seen from equation (2).

It can be shown also that the energy of shear associated with each particle sphere is proportional to $(G\epsilon)^2 \frac{4}{3}\pi r_0$.

This means that the energy is proportional to the volume $(\frac{4}{3}\pi r_0^3)$ of the particle and, therefore, the total elastic energy is also independent of the size of the particle.

The above calculations are limited to the case where the average distance of the particles is large compared with their size; that is, there is no mutual interaction of the particles, and it is calculated under the assumption that the particle is too big for the hole where it is situated, and that this misfit can be adjusted partly by compressing the particle and partly by an increase of the hole.

THE INFLUENCE OF PARTICLE SHAPE

The energy needed to enlarge a hole is greatest in the case of a spherical hole, decreases to about $\frac{3}{4}$ of this value if the sphere becomes a needle, and approaches zero for very flat plates. Thus the two terms, in Equation (1) constituting the increase of free energy due to the particles, show a different dependence on particle shape. The energy of shear is greater for a sphere than for a flat platelike particle, whereas the opposite is true in the case of the surface energy.

By using particles of a more or less uniform shape (spheres or plates), it should be possible to reproduce the two limiting cases and to find which is technically of greater importance to give a certain effect.

Probably the increase in the internal elastic energy is generally shown by the increased hardness of the resulting material, whereas the surface forces seemingly manifest themselves by producing a tougher structure.

There are also a number of other processes in which a rubber mix containing a filler behaves differently from the unfilled one. For instance, in the swelling of a filled material, the solvation forces have not only to overcome the forces between the rubber particles, but also the surface forces, and have to perform work against the internal elastic energy. It is, therefore, not surprising that filled rubber materials often exhibit a reduced swelling capacity.

The elastic energy effect is not confined to macroscopic particles, but exists also if the particles are of molecular dimensions and form a solid solution; on the contrary, one must expect that soluble impurities show an even greater influence than insoluble ones. The effect occurs in the volume of the material, and is again related to the distortion of the original lattice structure by the admixture. The impurities compress or expand the surrounding lattice, depending on whether their size is larger or smaller than that of the normal atoms or molecules which they are replacing. This effect may be of some importance in determining the mechanical properties of mixed plastics.

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THERMAL DECOMPOSITION OF NATURAL AND SYNTHETIC RUBBER STOCKS *

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The factors responsible for failure of natural and synthetic rubber stocks in tires in service are primarily thermal in nature. They govern the temperature attained by the stock and the ability of the stock to withstand this temperature. The factors which determine the temperature attained include those dependent upon the stock itself and those dependent upon attendant conditions. In the first group may be mentioned thermal conductivity, internal friction, and elastic modulus. In the second are included the construction and design of the tire, the speed at which it is run, the load to which it is subjected, its inflation pressure, and the temperature of the road and surrounding air. Therefore, assuming a fixed set of conditions for the second group, the problem resolves itself into a determination of the amount of heat generated within the stock, the rate at which the generated heat is conducted away from it, and the temperature it may attain without undergoing chemical degeneration. These characteristics can be investigated independently in the laboratory.

The first two characteristics have received considerable attention. Williams[1], Barnett[2], and Frumkin and Dubinker[3] are among those who have investigated the thermal conductivity. The problem of heat generation has been studied by Barnett and Mathews[4], Fielding[5], Jones and Pearce[6], and others, using the rebound technique to determine energy absorption; by Kosten[7], Naunton and Waring[8], Roelig[9], Sebrell and Dinsmore[10], Gehman *et al.*[11], using high-frequency vibrations; and by Cooper[12], Havenhill[13], Lessig[14], Mackay, Anderson, and Gardner[15], and Gough and Parkinson[16] in apparatus involving the destructive working of rubber stocks. The latter method gave results which included the combined effect of internal friction, elastic modulus, and thermal conductivity. The third characteristic, the chemical degeneration temperature, has received little attention in the literature. Its importance is evident when we realize that the primary consideration is not how cool a stock may run but, rather, the margin between the running temperature of the stock and its degeneration temperature. Thus, it is entirely possible for a given stock to run cooler than another stock and yet to degenerate more rapidly than the second stock because of the difference in the degeneration temperature of the two stocks. (Not considered are other materials in close proximity to the stock, such as cord fabric, which have their independent degeneration temperatures but may generate little heat themselves. Such materials reach their thermal degeneration temperature by virtue of the temperature attained by the stock. The ability of the stock to resist degeneration has, of course, no bearing on their thermal failure, although the degeneration of the stock may tend to hasten their failure from other causes, such as increased stress or separation.)

One definite indication of this chemical degeneration is the development of porosity in the stock. The point at which porosity or blowhole formation

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occurs in a stock may be defined as its decomposition temperature. It is readily conceded that some chemical degeneration may take place at a temperature below the decomposition temperature. In fact, any elevated temperature produces some change in both natural and synthetic rubber stocks. In a broad sense this change could be considered chemical degeneration. However, where rapid and complete stock failure is at issue, it appears reasonable to assume that the effective degeneration temperature approaches the decomposition temperature as defined.

Chemical degeneration, as considered here, is an internal phenomenon produced by the effect of heat alone on the stock. Failures such as sun checking or flex cracking are not considered. Thus, to exclude any possible effect of oxidation through contact with the air at elevated temperatures, the technique of submersion in a molten alloy was employed. This had the added advantage of heating the samples more rapidly and uniformly.

POROSITY METHOD FOR THERMAL DECOMPOSITION TEMPERATURE

The apparatus (Figure 1) consisted essentially of an insulated steel bar, 76.2 × 30.5 × 8.9 cm. (30 × 12 × 3.5 inches), containing cylindrical cavities 2.9 cm. in diameter and 6.35 cm. deep (1.14 × 2.5 inches) for the test-samples located in columns of six at ten regular intervals along its length, heater elements at one end, and a cooling chamber at the other. During actual tests it was found unnecessary to use the cooling chamber. The cavities were

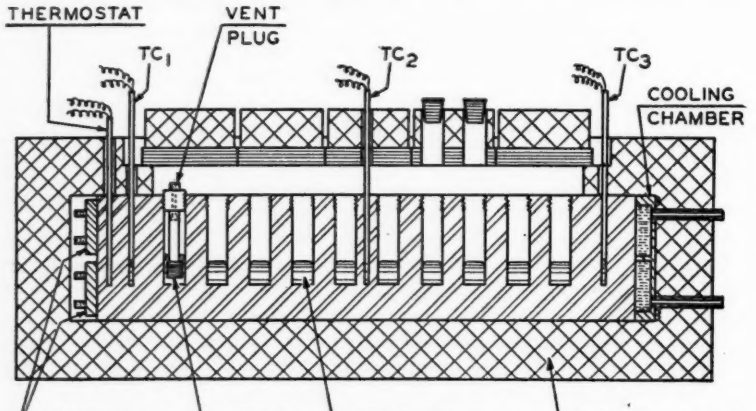

FIG. 1.—Thermal decomposition apparatus.

partially filled with a low-melting alloy. At test temperatures above 200° C, an alloy of 50.0 parts tin, 32.0 parts lead, and 18.0 parts cadmium was used. At lower temperatures it was necessary to add as much as 10 per cent mercury to the alloy to keep it from solidifying. Cube test-samples, 1.9 cm. (0.75 inch), were placed in the cavities and forced into the liquid alloy with threaded plugs. The plugs contained vent holes to allow escape of the air above the alloy in case of a blowout of the test samples. A bimetal thermal regulator was inserted in the bar near the heater end. Iron-constantan thermocouples were inserted into the base of alloy-filled cavities at points TC_1, TC_2, and TC_3.

The bar was insulated on the sides, ends, and bottom with 7.6 cm. (3 inches) of magnesia block. Lids of magnesia block and transite were provided, one for each pair of cavity columns. Corks were fitted into one of the lids so that the cavity plugs could be removed and test-samples inserted with a minimum of heat loss.

The apparatus was calibrated by measuring the temperature in each of the cavities by thermocouples after equilibrium thermal conditions were reached. Figure 2 shows the temperature gradient obtained. Since the temperatures

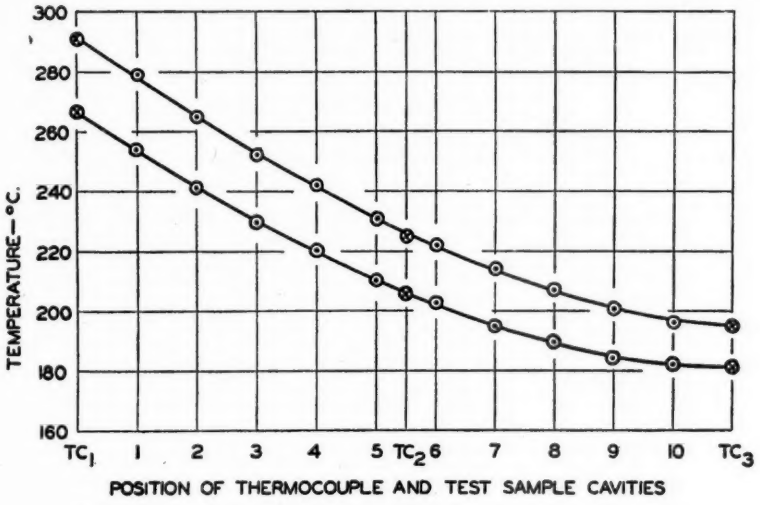

FIG. 2.—Typical temperature gradient curves of thermal decomposition bar.

of the three permanent points, TC_1, TC_2, and TC_3, were found to lie on the curve, these points were used to determine the cavity temperatures of actual tests by drawing a curve through them of the same general shape as the calibration curve. Temperature tests in each column in no case showed the temperature in the cavities of the two outside rows to be more than 2.0° C lower than the temperature in the cavities of the respective columns of the two center rows. At the cooler end of the bar, this differential was, in general, less than 1.0° C. Because these variations were considerably less than the difference from column to column, they were disregarded in obtaining the cavity temperatures of the tests.

The thermostat was adjusted to give the proper temperature at the heater end of the bar. After the bar reached thermal equilibrium, usually in 48 hours, the temperatures at TC_1, TC_2, and TC_3 were measured. The test-samples were then inserted, one at a time, with all cavities covered except the one being loaded. The samples were removed at the end of one hour in the same order in which they were loaded. The one-hour interval was selected after determinations were made which showed no change in the temperature of blowhole formation as a function of time in the interval 0.5 to 2 hours. The temperatures were remeasured just before removal. The average temperature reading at each position was used to obtain the temperature curve. After cooling, the samples were cut open to determine the presence of blowholes, splits, or other signs of heat failure.

TABLE I

FORMULAS AND CURES OF HEVEA RUBBER STOCKS

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
Smoked sheet	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Sulfur	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Zinc oxide	3	3	3	3	42.5	42.5	42.5	42.5	3.3	3.3	3.3	3.3	3.3	3.3	3.3
Channel black	...	...	...	...	...	...	...	...	50	50	50	50	50	50	50
Stearic acid	0.5	0.5	0.5	0.5	0.6	0.6	0.6	0.6	3.3	3.3	3.3	3.3	3.3	3.3	3.3
Pine tar	...	...	...	...	1.75	1.75	1.75	1.75	3.3	3.3	3.3	3.3	...	...	...
Paraflux	...	...	...	...	...	...	...	...	...	...	...	...	4.2	4.2	4.2
Antioxidant	...	...	...	...	1	1	1	1	1	1	1	1	1	1	1
D. O. T. G.	1.1	...	...	...	1.3	...	...	...	1.1	...	...	...	1.1	...	...
Captax	...	1.0	...	...	...	1.2	...	...	...	1.0	...	...	...	1.0	...
A-32	...	...	1.5	...	...	...	1.8	...	...	...	1.5	...	...	...	1.5
Santocure	...	...	...	0.7	...	...	...	0.85	...	...	...	0.7	...	...	...
Curing time at 148.9° C (300° F) (min.)	55	55	55	55	55	55	55	55	55	55	55	55	55	55	55

	P	Q	R	S	T	U	V	W	X	Y	Z	AA	BB	CC
Smoked sheet	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Sulfur	3	5	5	5	5	3.5	2.5	3	3	3	3	3	3	3
Zinc oxide	3.3	...	10	10	10	3.3	3.3	3.3	3.3	66.5	3	3	3	3
Channel black	50	...	...	...	...	50	50	40	25	...	18	...	...	...
Stearic acid	3.3	...	...	...	1	3.3	3.3	3.3	3.3	3	3	3	3	3
Pine tar	...	...	...	...	...	3.3	3.3	3.3	3.3	...	...	...	...	...
Antioxidant	4.2	...	...	...	...	1	1	1	1	...	...	...	...	...
Captax	1	...	...	1	1	1	1	1	1	1	1	1	1	1
Clay	...	...	...	...	...	...	...	...	...	...	...	26	...	....
Calcene	...	...	...	...	...	...	...	...	...	...	...	...	26	...
P-33	0.7	...	...	...	...	...	...	...	...	...	...	...	...	18
Curing time at 148.9° C (min.)	55	90	90	55	55	55	55	55	55	55	55	55	55	55

With the exception of the reclaim stocks, the formation of blowholes with rise in temperature was abrupt. An interval of 10° C was usually sufficient to separate a normal sample from one containing many holes of the order of 1.5 mm. in diameter. In the case of reclaim stocks about twice this interval was required. The temperature of the block was adjusted, by means of trial tests, so that blowhole formation occurred in the region from the middle to the cool end of the bar. In this region the temperature change from column to column averaged about 4° C. Therefore, by uniformly selecting, as the temperature of blowhole formation, that temperature at which small or pinholes first appeared, the actual decomposition temperature was in no case more than about 4° C lower than the recorded temperature of blowhole formation.

EVALUATION OF STOCKS

Tables I and II give the stock formulas and the curing times and temperatures. The cures selected were such as to overcure the stocks slightly rather than to undercure them. Thus any effect which might result from completing the cure of an undercured stock without the curing pressure was eliminated. The desirability of comparing series of stocks containing only one variable precluded the possibility of compounding the most desirable commercial stocks in all instances. Tables III to VIII give the decomposition temperatures, as

TABLE II

FORMULAS AND CURES OF STOCKS FOR BASE MATERIAL COMPARISON

	DD	EE	FF	GG	HH	II	JJ	KK	LL
Buna-S	100	...	...	...	...	...	...	...	...
Butaprene-NM	...	100	...	...	...	...	...	...	...
Butaprene-NXM	...	...	100	...	...	...	...	...	...
Neoprene-Gn	...	...	...	100	...	...	...	...	...
Smoked sheet	...	...	...	...	100	...	...	...	...
Whole-tire reclaim	...	...	...	...	...	175	...	...	...
Black-tube reclaim	...	...	...	...	...	...	150	...	...
Untreated guayule	...	...	...	...	...	...	...	100	...
Deresinated guayule	...	...	...	...	...	...	...	...	100
Sulfur	2	2	2	...	3	3	3	3.5	3.5
Zinc oxide	3	3	3	5	3	3	3	3	3
Stearic acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Captax	1.5	1.5	1.5	...	1	1	1	1	1
Antioxidant	...	...	...	2	...	...	...	...	...
Latac	...	...	...	0.2	...	...	...	...	...
Light-calcined magnesia	...	...	...	4	...	...	...	...	...
Altax	...	...	...	0.5	...	...	...	...	...
Curing time at 143.3° C (min.)	40	40	40	40	40	40	40	40	40

	MM	NN	OO	PP	QQ	RR	SS	TT	UU
Buna-S	100	...	...	...	...	...	...	...	...
Butaprene-NM	...	100	...	...	...	...	...	...	...
Butaprene-NXM	...	...	100	...	...	...	...	...	...
Neoprene-GN	...	...	...	100	...	...	...	...	...
Smoked sheet	...	...	...	...	100	...	...	...	...
Whole-tire reclaim	...	...	...	...	...	175	...	...	...
Black-tube reclaim	...	...	...	...	...	...	150	...	...
Untreated guayule	...	...	...	...	...	...	...	100	...
Deresinated guayule	...	...	...	...	...	...	...	...	100
Sulfur	2	2	2	...	3	3	3	3.5	3.5
Zinc oxide	3	3	3	5	3	3	3	3	3
Channel black	50	50	50	36	50	24	43	50	50
Stearic acid	3	3	3	1	3	3	3	1	1
Bardol	6	6	6	...	3.5	3.5	3.5	...	...
Captax	1.5	1.5	1.5	...	1	1	1	1.5	1.5
Antioxidant	...	...	...	2	1	1	1	1	1
Latac	...	...	...	0.5	...	...	...	...	...
Light-calcined magnesia	...	...	...	4	...	...	...	...	...
Altax	...	...	...	0.75	...	...	...	...	...
Cottonseed oil	...	...	...	2.5	...	...	...	...	...
Curing time at 143.3° C (min.)	45	45	45	45	45	45	45	45	45

Table III

Effect of Accelerators in Hevea Rubber Stocks

Accelerator	Temperature of blowhole formation: Gum stock No.	Gum stock °C	Carcass stock No.	Carcass stock °C	Tread stock with pine tar No.	Tread stock with pine tar °C	Tread stock with paraflux No.	Tread stock with paraflux °C
D. O. T. G.	A	177	E	173	I	174	M	174
Captax	B	198	F	199	J	201	N	199
A-32	C	177	G	173	K	174	O	173
Santocure	D	191	H	185	L	195	P	184

Table IV

Effect of Basic Ingredients in Hevea Rubber Stocks

Ingredients of *Hevea* stock	Temp. of blowhole formation No.	°C
Sulfur[a]	Q	192
Sulfur + ZnO	R	182
Sulfur + ZnO + Captax	S	191
Sulfur + ZnO + Captax + stearic acid	T	194

[a] The rubber-sulfur stock was slightly undercured, but tests at higher cures showed negligible variation.

Table V

Effect of Sulfur Content of Hevea Rubber Stocks

Parts sulfur/100 parts rubber (by wt.)	Temp. of blowhole formation No.	°C
2.5	V	213
3.0	J	199
3.5	U	200

Table VI

Effect of Channel Black Loading on Hevea Rubber Stocks

Parts channel black/100 parts rubber (by wt.)	Temp. of blowhole formation No.	°C
0	B	198
18	Z	201
25	X	198
40	W	204
50	J	203

Table VII

Effect of Pigments in Hevea Rubber Stocks

Ten parts pigment/100 parts rubber (by vol.)	Temp. of blowhole formation No.	°C
Zinc oxide	Y	201
Channel black	Z	201
Clay	AA	209
Calcene	BB	193
P-33	CC	219

TABLE VIII

COMPARISON OF BASE MATERIALS

Base material	Temperature of blowhole formation			
	Gum type stock		Tread type stock	
	No.	°C	No.	°C
Buna-S	DD	254	MM	233
Butaprene-NM	EE	248	NN	244
Butaprene-NXM	FF	248	OO	233
Neoprene-GN	GG	227	PP	233
Smoked sheet	HH	198	QQ	198
Whole-tire reclaim	II	146	RR	157
Black-tube reclaim	JJ	159	SS	157
Untreated guayule	KK	143	TT	138
Deresinated guayule	LL	150	UU	153

TABLE IX

EFFECT OF CURE ON TYPICAL TREAD STOCKS

Curing time at 143.3° C (min.)	Temperature of blowhole formation (° C)		
	Hevea rubber (QQ)	Buna-S (MM)	Deresinated guayule (UU)
25	187	187	155
45	197	228	155
65	202	232	155
85	...	232	155
105	...	...	155
125	...	...	155

indicated by the temperature of blowhole formation, of the stocks studied. Table IX gives the effect of time of cure on some of these stocks.

Hevea rubber stocks.—In all types of stocks (tread, carcass, and gum) Captax, followed by Santocure, was found to be superior to D. O. T. G. and A-32 (aldehyde-amine type) accelerators (Table III).

No significant difference was found between pine tar and Paraflux in tread stocks (Table III).

The introduction of zinc oxide to a rubber-sulfur mix reduced the decomposition temperature. The introduction of Captax and Captax plus stearic acid to the rubber-sulfur-zinc oxide mix produced a rise in the decomposition temperature to that of the rubber-sulfur mix (Table IV).

Low-sulfur (2.5 parts by weight on 100 parts of rubber) tread stock was found to have a higher decomposition temperature than medium (3.0 parts) and high (3.5 parts) sulfur tread stocks (Table V).

In the channel black series, the stocks with low loadings of black had a slightly lower decomposition temperature than the stocks with loadings of 40 and 50 parts by weight on 100 parts of rubber (Table VI).

In the pigment series, P-33 black, followed by clay, had the highest decomposition temperature, zinc oxide and channel black were intermediate, and Calcene was lowest (Table VII).

Base material.—In the gum type stocks, the Buna types (butadiene copolymers) were found to have the highest decomposition temperature, followed by Neoprene-GN, *Hevea*, reclaim and guayule rubber in that general order (Table VIII).

In the tread type stocks, the Buna types and Neoprene-GN had the highest decomposition temperature, followed by *Hevea*, reclaim, and guayule rubber in that general order (Table VIII).

Stocks containing deresinated guayule had a somewhat higher decomposition temperature than those containing untreated guayule (Table VIII).

In the case of the guayule stocks, the decomposition temperature approached the curing temperature (Table VIII). In fact, in the case of the tread stock containing the untreated guayule, the decomposition temperature was actually lower than the curing temperature. Apparently the curing pressure was the only thing that prevented this stock from developing blowholes during cure. Presumably the curing temperature was not maintained a sufficient time after removal of the curing pressure to allow blowholes to form.

In the case of some of the Buna type stocks, separation in the form of cracks or splits occurred at temperatures lower than those necessary to produce decomposition as evidenced by blowholes. Thus, in the case of the Buna-S gum stock, the decomposition temperature as reported was 254° C, and splits occurred at 238° C. In the case of the tread stocks, Buna-S decomposed at 233°, split at 216° C; Butaprene-NM decomposed at 244°, split at 187° C; Butaprene-NXM decomposed at 233°, split at 209° C. It is believed that this separation occurred between the plies introduced in preparing the stock for the curing of the blocks from which the test-samples were taken. It is doubtful if these cracks would appear in the case of extruded stock. This point was not investigated.

Effect of cure.—The effect of variation of the time of cure is given for only three of the stocks studied (Table IX) for the sake of brevity. The effect was greatest for the Buna-S tread stock, MM, whereas no effect was apparent for the guayule tread stock, UU. Other stocks tested showed smaller effects than that for stock MM. In all cases the temperature of blowhole formation became nearly constant for times at and above the optimum cure (as determined by tensile strength). All cures used in Tables III to VIII were at or slightly over the optimum, except in one case noted in Table IV.

SIGNIFICANCE OF RESULTS

It is apparent that a wide range of decomposition temperatures exists between different stocks. At present the practical significance of these occasional large differences in decomposition temperature is not entirely known. It is interesting to note, however, the implication of the result that Captax-accelerated natural rubber stocks yield over 20° C higher decomposition temperatures than stocks accelerated with D. O. T. G. This result may at least partially explain the superior resistance to abrasion imparted by Captax compared with D. O. T. G., a result not completely obvious from physical tests. Similarly, the much higher decomposition temperatures shown by the Buna-type synthetic and Neoprene-GN compared to natural rubber appears consistent with their satisfactory performance in tires, even with the higher running temperatures which they produce. Knowledge of the physical properties of synthetic rubber stocks hardly allows prediction of this result with certainty.

This test is referred to the chemist, to be employed as a compounding guide in the consideration of one factor governing the suitability of stocks in the light of the applications for which they are intended. Although most of the compounds studied were of the type used in conventional tire manufacture, the possible applications of the study of thermal decomposition to stocks designed for many other uses where heat becomes a factor are evident.

ACKNOWLEDGMENT

The author wishes to thank O. D. Cole for compounding the stocks studied in this paper and J. W. Liska for his many helpful suggestions concerning standardization of the apparatus. The guidance of J. H. Dillon and the continued interest of J. N. Street in the course of this work is greatly appreciated. The permission of the Firestone Tire and Rubber Company to publish this work is gratefully acknowledged.

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SOME DYNAMIC PROPERTIES OF RUBBER*

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PREVIOUS WORK

Kosten[2] tested massive rubber cylinders under forced vibrations. Three ratios of diameter to length were used, namely, 1, $\frac{1}{2}$, and $\frac{1}{4}$. All were tested in compression. He assumed a viscous damping, and found that the product of frequency and damping coefficient was constant. He introduced the angle of loss as a variable. It is defined as $\tan^{-1}\frac{cp}{k}$, where c, p, and k represent damping coefficient, angular frequency, and spring constant, respectively. He concluded that:

1. The modulus of elasticity, as calculated from dynamic tests, is larger than the static modulus.
2. The dynamic modulus is independent of frequency.
3. The angle of loss has a tendency to increase with frequency and load.

Naunton and Waring[3] used a moving-coil driver unit which applied an alternating stress to two cylinders of rubber, each having a diameter of twice the length, placed on either side of a diaphragm attached to the moving coil. The system was tuned to resonance, and all calculations were made from measurements of amplitude and frequency at resonance. The following conclusions were reached:

1. The dynamic modulus of elasticity tends to increase with frequency.
2. The viscous resistance decreases with frequency and tends to become constant at higher frequencies.

Roelig[4] tested cylinders of rubber bonded to metal disks at the ends. The diameter and length were equal in all cases. A coil spring maintained a static load, and a dynamic load was superposed on this by means of an eccentric weight on the shaft of an electric motor. The load was measured by means of a dynamometer, and the displacement was taken as equal to that of the motor. A beam of light was reflected from two mirrors, one mounted on the casing of the motor and one in the dynamometer. This beam of light described a dynamic hysteresis loop on which calculations were based. Quantities measured include:

(1) Δw = energy lost per cycle (area of hysteresis loop).

(2) $\frac{\Delta w}{w}$ = ratio of energy lost to total energy (loop area divided by area between loop and axis of strain).

(3) Dynamic modulus of elasticity.

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Roelig concluded that:

(1) Δw increases with increase of dynamic load while $\frac{\Delta w}{w}$ remains constant.

(2) Δw decreases with increase of static load while there is not much change in $\frac{\Delta w}{w}$.

(3) Both Δw and $\frac{\Delta w}{w}$ show a slight increase with increase of frequency.

(4) Δw increases with volume while $\frac{\Delta w}{w}$ decreases.

Of interest in regard to internal damping is a paper by Williams[5], who states: "Energy expended on raw or vulcanized rubber is consumed largely by producing plastic flow and reversible elastic strain. . . . Stress-strain curves obtained rapidly become straight lines through elimination of plastic flow." From this it would be expected that Δw would decrease with increase of frequency.

HYSTERESIS AND INTERNAL DAMPING

The energy lost by a unit volume of material in passing through a cycle of stress is equal to the area of the hysteresis loop. On the assumption that this loop maintains a constant shape, the area is proportional to ϵ_0^2, where ϵ_0 is the amplitude of strain. The area may be taken as $F\epsilon_0^2$, term F being a factor dependent on material, type of stress, etc. For a bar of constant cross-section, which has the same stress throughout its length, the total loss in energy is $F\epsilon_0^2$ times the volume, or $F\epsilon_0^2 Al$.

For a member of length l, with one end stationary and the other end subjected to a cyclic displacement of amplitude x_0, the damping force, taken as proportional to the velocity of the moving end, is Cx. The work done by the damping force in one cycle is $\pi C p x_0^2$ where p is the angular frequency of the motion. Equating this to the total hysteresis loss:

$$\pi C p x_0^2 = F\epsilon_0^2 Al = F x_0^2 \frac{A}{l}$$

$$\frac{Cl}{A} = \frac{F}{\pi p} = C_2 \tag{1}$$

Coefficient C_2 appears to be very convenient for use in specifying internal damping, since it permits comparison of specimens of different dimensions. Its physical significance may be seen by writing $C = C_2 \frac{A}{l}$, from which the damping force is $C_2 \frac{A}{l} x = C_2 A \epsilon$. Thus, C_2 is a damping coefficient which is to multiply the velocity of strain and the area to give the damping force. Its units are $\frac{\text{lb-sec}}{\text{in.}^2}$. All damping data obtained in this investigation have been expressed by means of C_2. Equation (1) indicates that C_2 is inversely proportional to the frequency, if the hysteresis loop maintains the same shape at all frequencies. Any deviation of C_2 from such inverse proportionality would indicate that the frequency has an effect on the shape of the hysteresis

loop. If different values of C_2 are obtained for specimens of different shape, this would indicate a dependence of the condition of stress on the shape.

APPARATUS AND MEASUREMENTS

A dynamic loading was superposed on a static loading for a pair of specimens by means of a pendulum supported by an elastic hinge. A general view of the equipment is shown in Figure 1. In this system, the rubber contributed to the damping and to the spring constant.

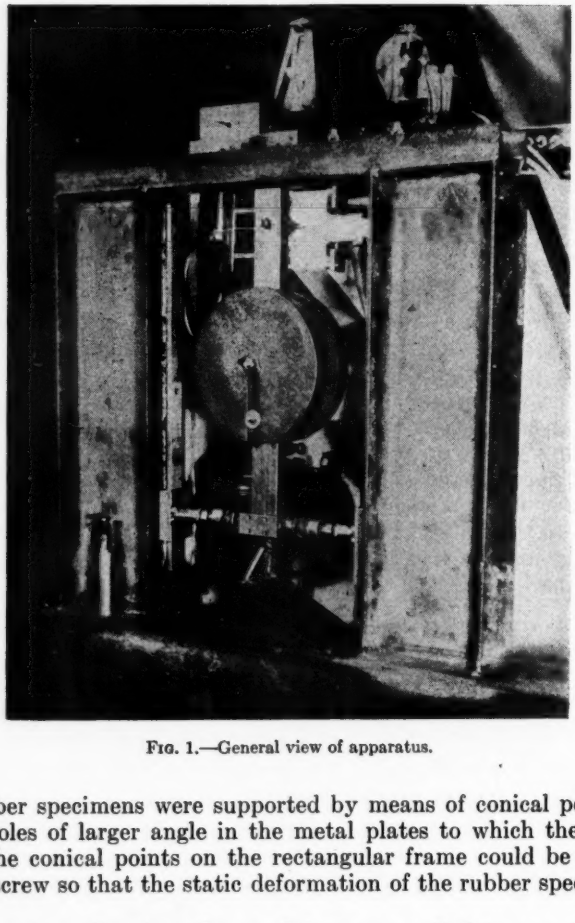


FIG. 1.—General view of apparatus.

The rubber specimens were supported by means of conical points seating in conical holes of larger angle in the metal plates to which the rubber was bonded. The conical points on the rectangular frame could be adjusted by means of a screw so that the static deformation of the rubber specimens could be varied.

To start a free vibration, the pendulum was pulled to one side and held by means of a pin. On pulling out the pin, the pendulum would oscillate in a free vibration. The initial amplitude of the motion could be varied by adjusting the bar which held the pin.

The motion of the pendulum was recorded on a strip of paper which moved across a metal plate. A needle A, on the end of the pendulum, discharged a high-frequency spark through the paper to the plate. The holes burned in

the paper by the spark constituted the record of the motion. In addition, a second needle B discharged a series of sparks each second, giving a time measure. The two needles are shown in their positions adjacent to the paper strip in Figure 2.

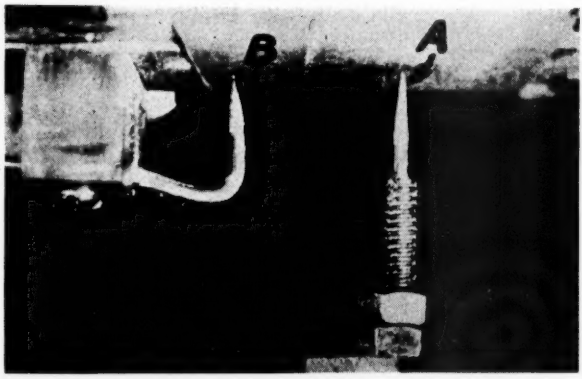


FIG. 2.—High-frequency-spark needles for recording motion of pendulum and time.

The frequency of the pendulum could be varied appreciably in three ways:

1. By changing the distance of the rubber specimens from the axis of rotation of the pendulum.
2. By adding auxiliary springs to the system.
3. By adding weights to the pendulum. One pair of weights appears in Figure 1.

The natural frequency of the pendulum alone varied from 1.15 to 34.8 cycles per second. The lowest frequency recorded for a vibration with rubber specimens was 3.93 cycles per second; the highest was 46.2 cycles per second.

The forces acting on the pendulum alone are shown in Figure 3 (a). The moment about the axis of rotation exerted by the elastic hinge is proportional to the angular displacement and is $-k\theta$. If the damping is taken as proportional to the angular velocity of the pendulum, the moment due to damping is $-k_1\dot{\theta}$. The equation of motion for the pendulum is:

$$I_0\ddot{\theta} = W\bar{r}\theta - k\theta - k_1\dot{\theta} \tag{2}$$

Since the linear displacement x is the quantity measured, it is best to change variables. For small displacements:

$$\theta = \frac{x}{l}; \quad \dot{\theta} = \frac{\dot{x}}{l}; \quad \ddot{\theta} = \frac{\ddot{x}}{l}$$

Substituting:

$$\ddot{x} + \frac{k_1}{I_0}\dot{x} + \frac{(k - W\bar{r})}{I_0}x = 0$$

This equation can be changed to standard form by letting $2q = \frac{k_1}{I_0}$ and $p^2 = \frac{k - W\bar{r}}{I_0}$. Then:

$$\ddot{x} + 2qx + p^2\dot{x} = 0 \tag{3}$$

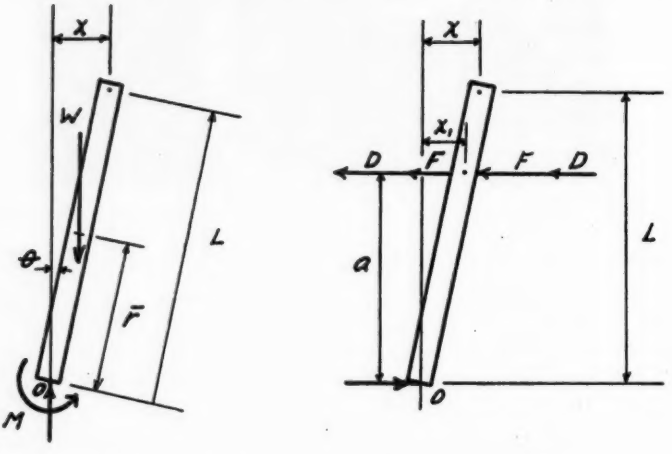
The solution of Equation (3) is:

$$x = x_0 e^{-qt}\left(\cos\sqrt{p^2 - q^2}\,t + \frac{q}{\sqrt{p^2 - q^2}}\sin\sqrt{p^2 - q^2}\,t\right)$$

in which x_0 is the initial amplitude. For the small damping encountered in this investigation, this is approximately:

$$x = x_0 e^{-qt}\cos pt \tag{4}$$

When two rubber specimens are added to the system, elastic forces F and damping forces D are exerted on the pendulum, Figure 3 (*b*). The elastic



(*a*) (*b*)

FIG. 3.—Forces acting on pendulum.
(*a*, Forces acting on pendulum alone; *b*, additional forces due to rubber specimens.)

force for each specimen is $F = \frac{Ex_1A}{l}$, or since $x_1 = \frac{ax}{L}$ then $F = \frac{EAa}{Ll}x$. The quantities E, A, and l are, respectively, modulus of elasticity, area, and length of the specimen. The inner end of the rubber specimen has the same velocity as the point on the pendulum at the distance a from the axis. The outer end is at rest. Assuming that the damping force D is proportional to the velocity of the moving end:

$$D = C\dot{x}_1 \quad \text{or} \quad D = C\frac{a}{L}\dot{x}$$

The additional moment due to the rubber specimens is:

$$-2\frac{EAa^2}{Ll}x - 2C\frac{a^2}{L}\dot{x}$$

When these terms are added to Equation (2), the following equation can be obtained:

$$\ddot{x} + \left(2q + 2\frac{Ca^2}{I_0}\right)\dot{x} + \left(p^2 + 2\frac{EAa^2}{I_0 l}\right)x = 0$$

Putting

$$2q_1 = 2q + 2\frac{Ca^2}{I_0} \tag{5}$$

and

$$p_1^2 = p^2 + 2\frac{EAa^2}{I_0 l} \tag{6}$$

$$\ddot{x} + 2q_1\dot{x} + p_1^2 x = 0$$

This has for an approximate solution:

$$x = x_0 e^{-q_1 t} \cos p_1 t \tag{7}$$

Equation (7) represents a cyclic motion with decaying amplitude. It has the period $\frac{2\pi}{p_1}$. The damping was measured in this investigation by means of the relation:

$$N = \frac{\text{Amplitude after } n \text{ cycles}}{\text{Initial amplitude}} = e^{-2\pi n q_1/p_1} \tag{8}$$

The manner of using it was as follows:

Equation (8) was plotted on semilogarithmic paper (on which it is a straight line) for several values of n, Figure 4. The quantity N was determined from the record of the vibration for the same values of n. Then each N was plotted on the proper line in Figure 4. If points so plotted fall in a vertical line, the

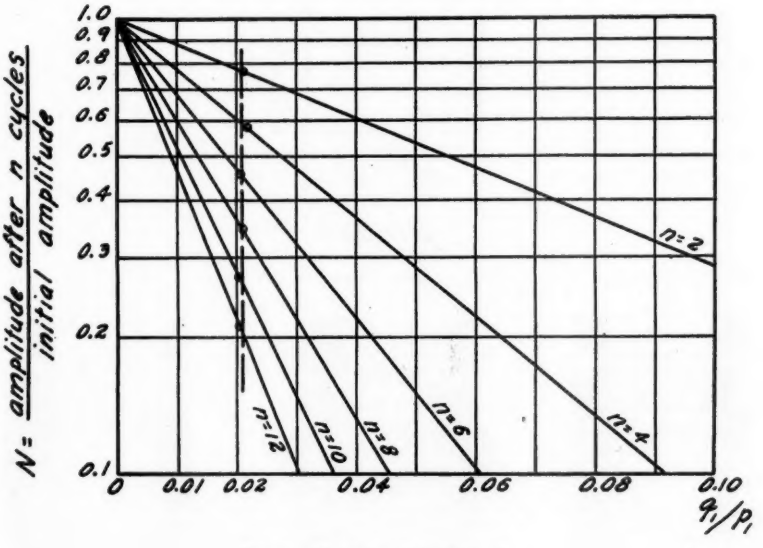


FIG. 4.—Chart for evaluating q_1/p_1.

damping force is proportional to the velocity, and the value of q_1/p_1 can be determined immediately. For each test performed in this investigation, the points plotted, as in Figure 4, could be represented reasonably by a vertical

line. The quantity n was increased in increments of 1, 2, or 10, depending on the rate at which the oscillation died out. The frequency, in cycles per second, of the motion described by Equation (7) can be obtained easily from the vibration record. If this frequency is denoted by f, then $p_1 = 2\pi f$. Term q_1 is the product of q_1/p_1 and p_1. The quantities q and p for the pendulum alone can be determined in the same way as q_1 and p_1. Then from Equations (5) and (6):

$$C = \frac{I_0}{a^2}(q_1 - q)$$

and

$$E = \frac{I_0 l}{2Aa^2}(p_1^2 - p^2)$$

From Equation (1), the damping coefficient C_2 in terms of which the damping data herein obtained have been expressed is $C_2 = \frac{Cl}{A}$.

CYLINDERS IN COMPRESSION

Results are given in the following section for seventeen pairs of cylinders tested in compression. These include cylinders of 1 in. diam. and lengths of 1 in. (3 pairs), 0.9 in., 0.8 in., 0.7 in., 0.6 in., 0.5 in., 0.4 in., 0.31 in., and 0.21 in.; 1.5 in. diam. and lengths of 1.05 in., 0.45 in., and 0.35 in.; 2 in. diam. and

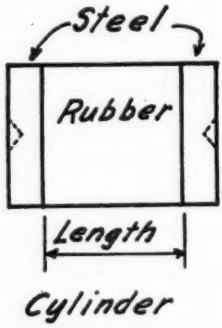


FIG. 5.—Type of test cylinder.

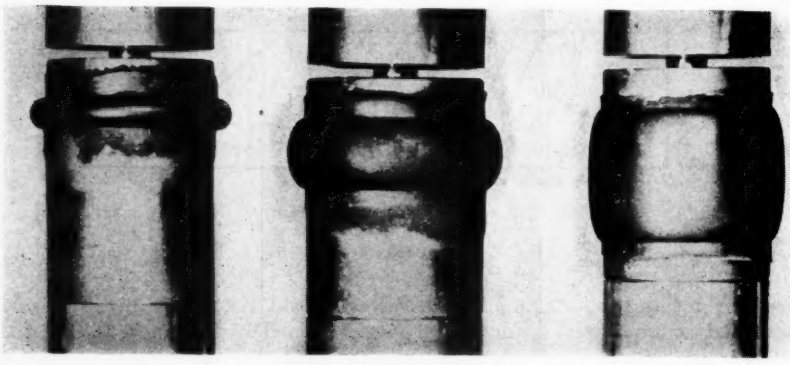


FIG. 6.—Three 1-in. cylinders.

lengths of 1.05 in., 0.45 in., and 0.35 in. All were bonded to steel disks at the ends, and were of the type shown in Figure 5. Figure 6 shows three cylinders of 1 in. diam. under a strain of approximately 0.25. A pronounced end effect, which depends on length, is evident. This made it desirable to test cylinders of several lengths for each diameter.

DAMPING OF CYLINDERS IN COMPRESSION

Figure 7 shows the effect of frequency on the damping coefficient C_2 for a number of the cylinders tested. The results indicate that the damping is inversely proportional to $f^{0.83}$. Additional results are given in Table 1.

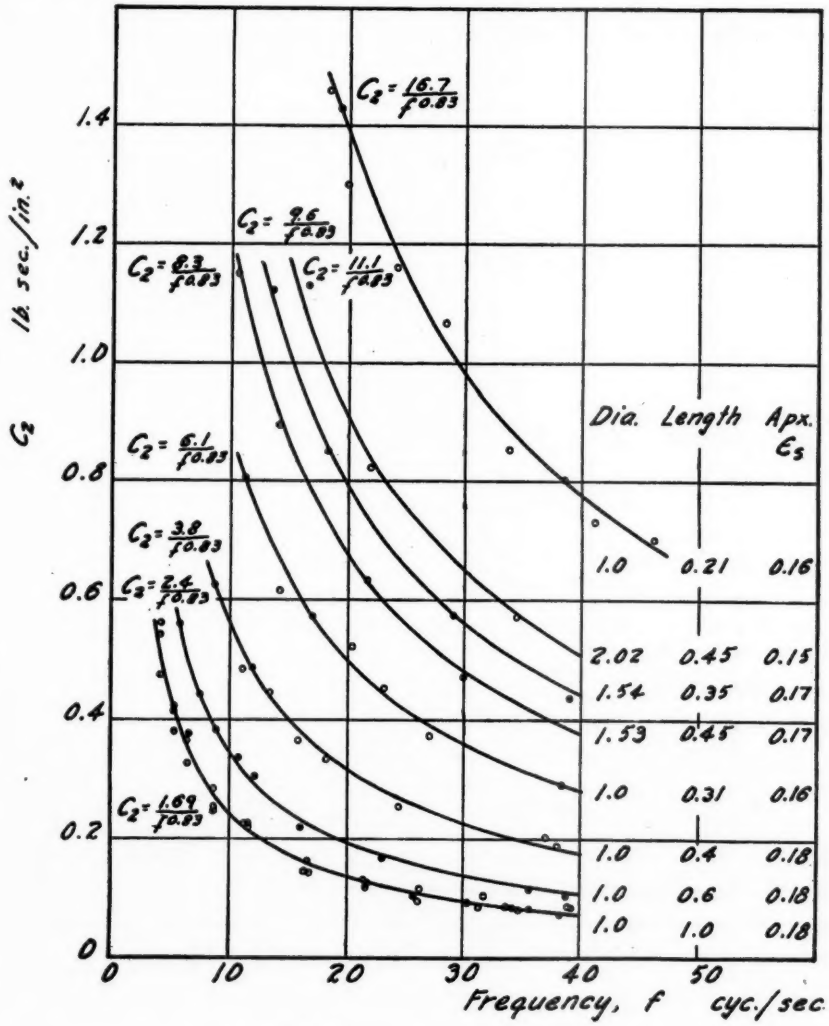


FIG. 7.—Effect of frequency on damping coefficient C_2.
(Cylinders in compression; ϵ_s = static strain.)

TABLE 1

RESULTS OF DAMPING TESTS

Diameter (in.)	Length (in.)	Approx. ϵ_s	$C_2 f^{0.83}$
1	0.9	0.18	1.64
1	0.5	0.18	2.47
1	0.7	0.18	1.76
1	0.8	0.14	1.76
2	1	0.15	2.12
2	0.35	0.15	16.5
1.5	1	0.17	1.65

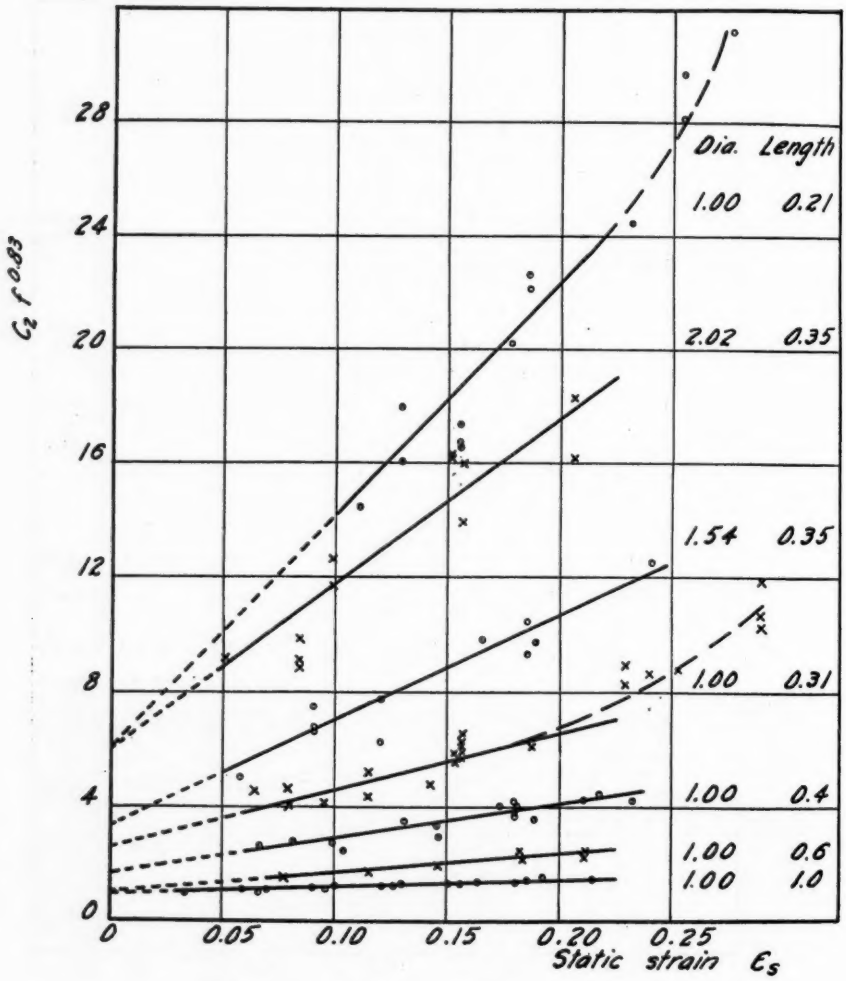


FIG. 8.—Effect of static strain on damping coefficient C_2.
(Cylinders in compression.)

The effect of static strain ϵ_s on the damping can be expressed by means of a function $A(\epsilon_s)$. Thus:

$$C_2 = \frac{A(\epsilon_s)}{f^{0.83}} \quad \text{or} \quad C_2 f^{0.83} = A(\epsilon_s)$$

Figure 8 shows the product $C_2 f^{0.83}$ plotted against the static strain for several pairs of cylinders. It appears that a linear relation is satisfactory for values of ϵ_s not exceeding 0.20, that is, $C_2 f^{0.83} = B_0 + B_1 \epsilon_s$, where B_0 is the intercept of the straight line on the vertical axis and B_1 is the slope.

The foregoing results indicate that the configuration of the cylinder has a considerable effect on the damping. A convenient way of describing the configuration is by means of the diameter-length ratio, d/L. Accordingly, the factors B_0 and B_1 from Figure 8 have been plotted against d/L in Figure 9.

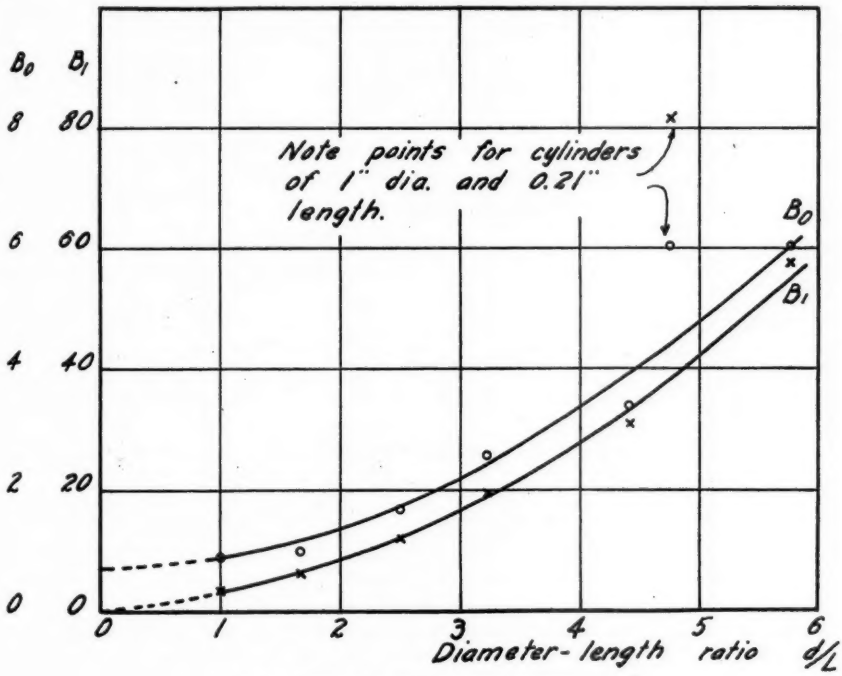


FIG. 9.—Factors B_0 and B_1 plotted against d/L.
(Cylinders in compression.)

The factors for the cylinders of 1 in. diam. and 0.21 in. length have values which are inconsistent with those for the other cylinders. This may be due to the $\frac{1}{32}$-in. layer of harder stock at each end. For this length, over 30 per cent of the specimen consists of the harder stock.

DYNAMIC MODULUS OF ELASTICITY

Figure 10 shows the modulus of elasticity, as determined from the dynamic tests, plotted against frequency. In this range, the frequency appears to have no effect upon the dynamic modulus.

The effect of static strain upon the dynamic modulus is shown in Figure 11. The results may be represented as:

$$E_{dyn} = E_0 + E_1\epsilon_s$$

for ϵ_s not exceeding 0.2.

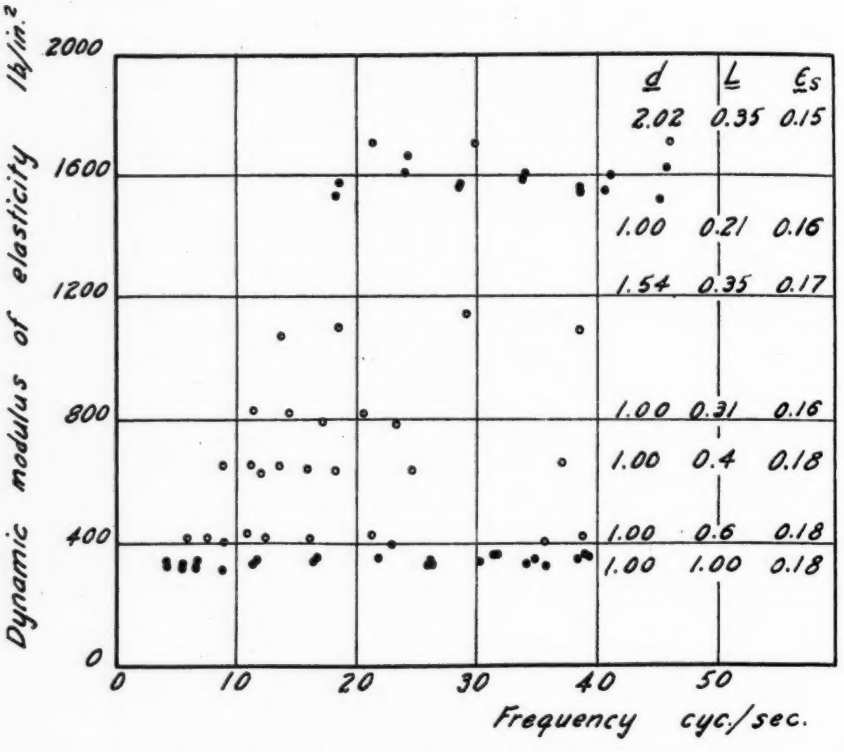


FIG. 10.—Effect of frequency on dynamic modulus of elasticity.
(Cylinders in compression. d = diameter, L = length, ϵ_s = approximate static strain.)

Figure 12 shows the effect of diameter-length ratio on the factors E_0 and E_1.

Static stress-strain curves for some of the cylinders are shown in Figure 13, in which the dynamic modulus of elasticity is shown in comparison with the static modulus. The short straight lines represent values of the dynamic modulus. In each case, the line has been drawn to intersect the static curve at the appropriate value of the static strain. It is evident that the dynamic modulus is slightly larger than the static modulus.

SHEAR SPECIMENS

Three pairs of specimens were tested in shear. All had the dimensions shown in Figure 14. Figure 15 shows a shear specimen under a static strain of approximately 1. There is no extreme end effect such as that seen in the cylinders in Figure 6. The block D was added after moulding, and was held in place by means of dowel pins and machine screws. The dimension l was

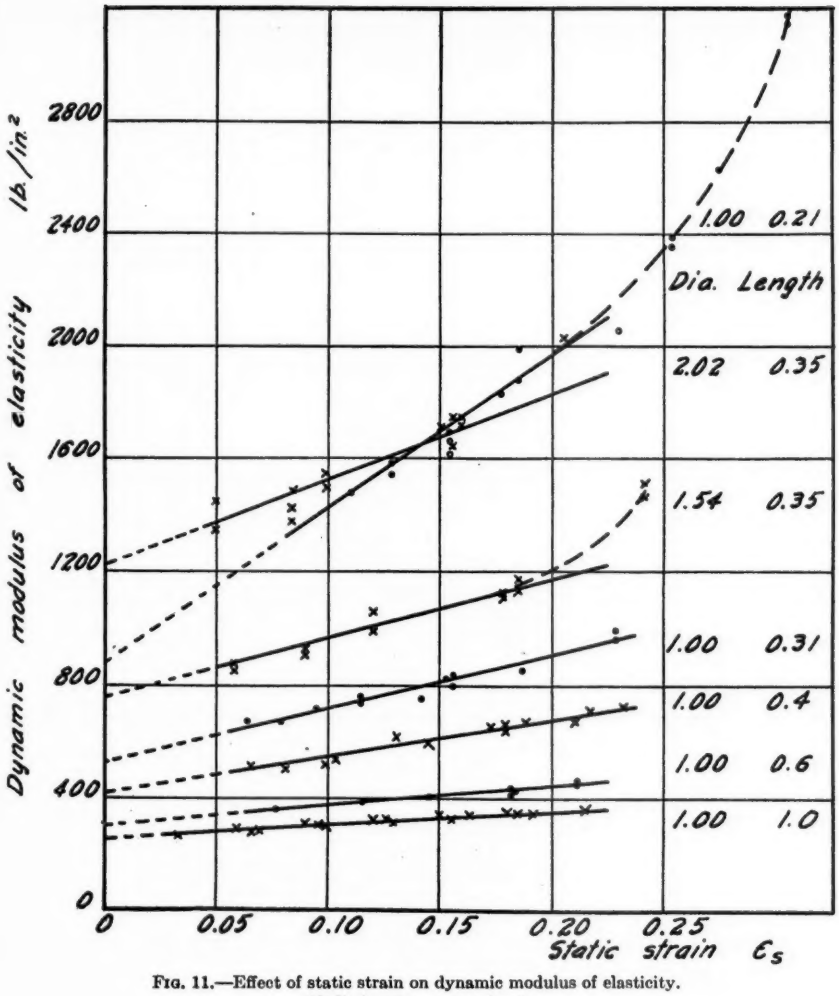


FIG. 11.—Effect of static strain on dynamic modulus of elasticity.
(Cylinders in compression.)

between 0.26 and 0.27 in. after moulding. By means of the machine screws, this was brought down to 0.25 in. The latter value was used in calculations.

DAMPING OF CYLINDERS IN SHEAR

The effect of frequency on the damping coefficient C_2 for the shear specimens is shown in Figure 16, from which it appears that the damping is inversely proportional to $f^{0.77}$.

In Figure 17, the product $C_2 f^{0.77}$ has been plotted against the static strain ϵ_s:

$$C_2 f^{0.77} = 0.15 + 0.05\epsilon_s$$

$$C_2 = \frac{0.15 + 0.05\epsilon_s}{f^{0.77}}$$

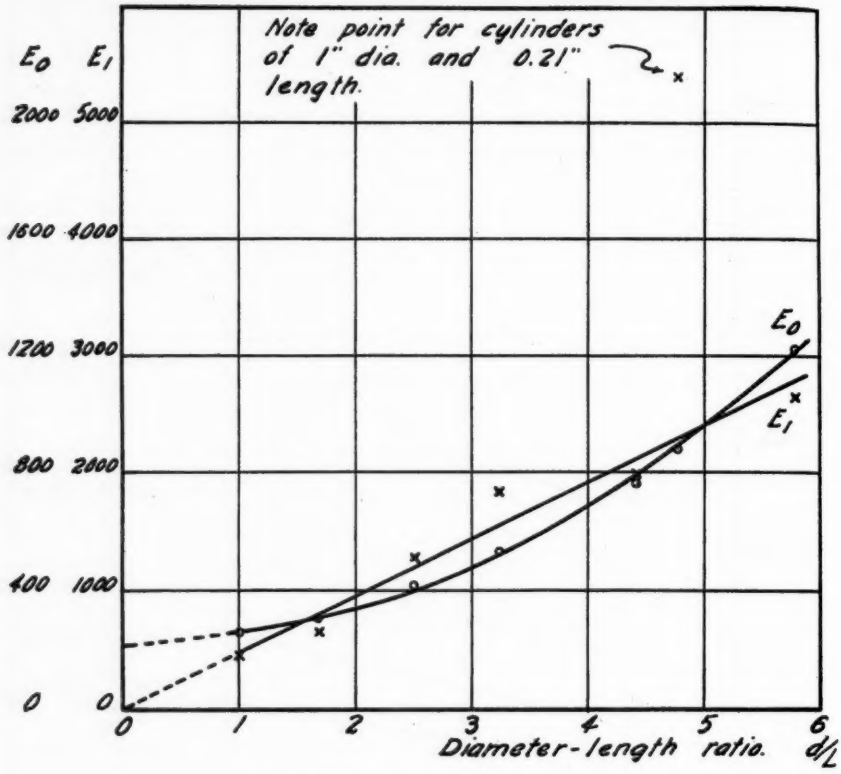


FIG. 12.—Effect of a/L upon factors E_0 and E_1.
(Cylinders in compression.)

DYNAMIC MODULUS OF ELASTICITY

The dynamic modulus of elasticity for the shear specimens is shown plotted against frequency in Figure 18. The results indicate that frequency has no effect upon the dynamic modulus.

Figure 19 shows the effect of static strain on the dynamic modulus. The results may be represented by:

$$E_{dyn} = 53 - 5.3\epsilon_s$$

Figure 20 shows an average static stress-strain curve for the six shear specimens, and a comparison between the dynamic modulus of elasticity and the static modulus. The short straight lines indicate values of the dynamic modulus, each line being drawn to intersect the static curve at the appropriate static strain. The dynamic modulus is slightly higher than the static modulus.

COMPARISON WITH PREVIOUS WORK

In regard to damping, the results stated for cylinders in compression agree fairly well with the conclusions of Kosten[2] and Naunton and Waring[3]. To

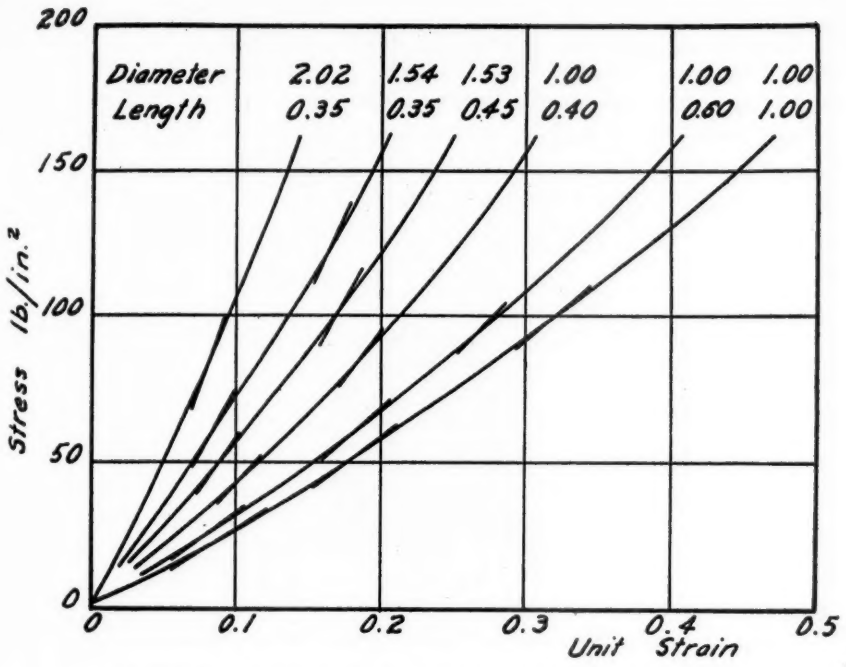


FIG. 13.—Comparison of dynamic modulus of elasticity with static modulus. (Cylinders in compression.)

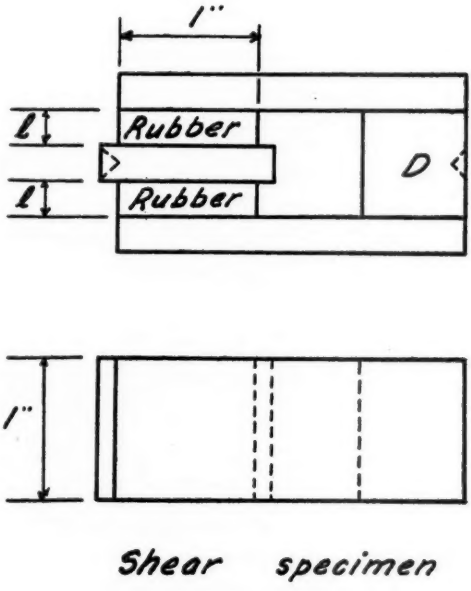


FIG. 14.—Shear specimen.

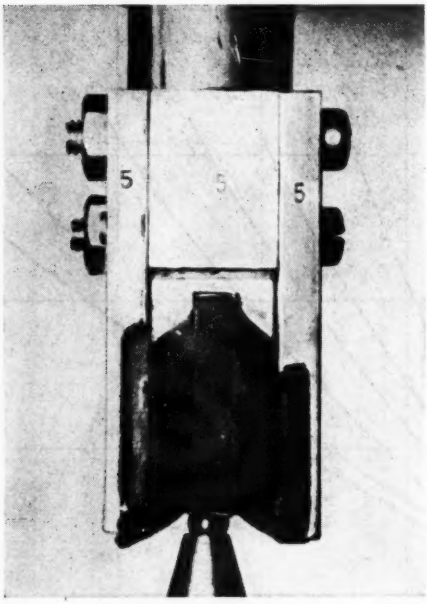


FIG. 15.—Shear specimen under static strain of approximately 1.

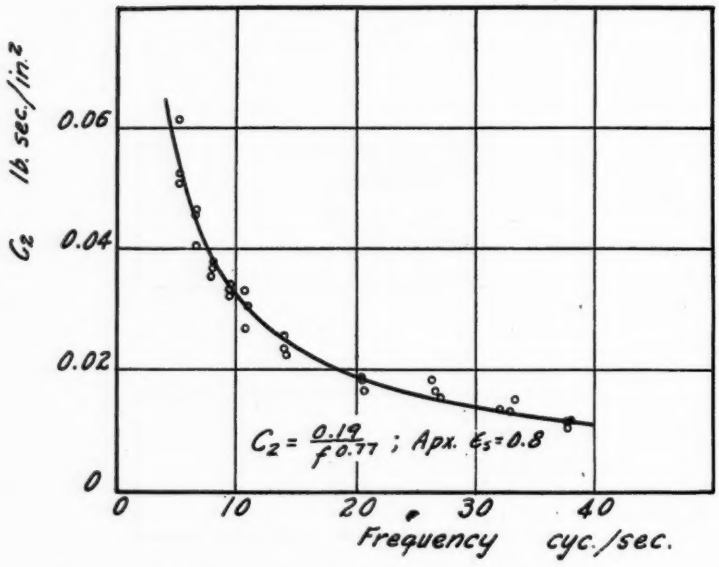


FIG. 16.—Effect of frequency on damping coefficient C_2 for shear specimens.

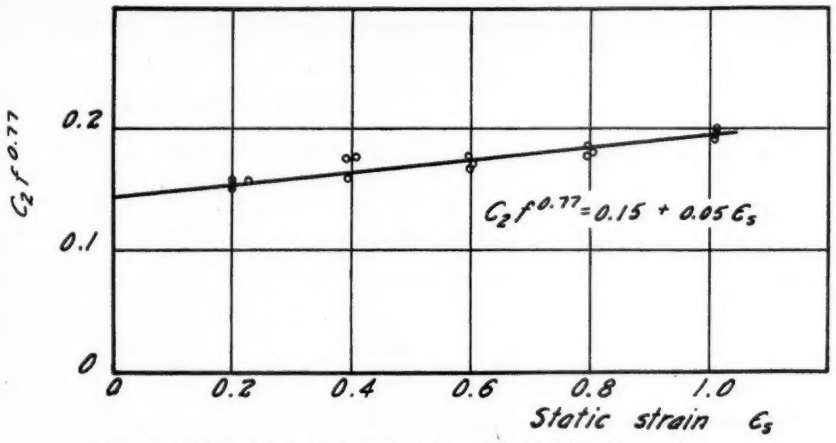


FIG. 17.—Effect of static strain on damping coefficient C_2 for shear specimens.

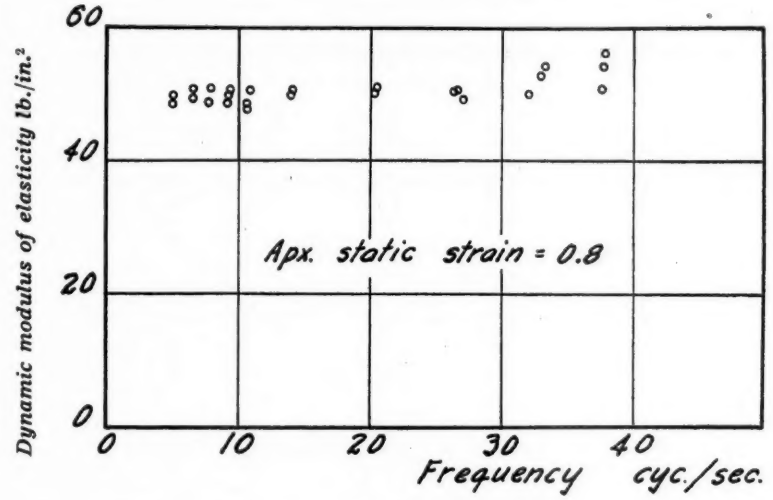


FIG. 18.—Effect of frequency on dynamic modulus of elasticity for shear specimens.

compare with Roelig[4], it is necessary to express the results in terms of energy. Since all of Roelig's tests were made on cylinders having a diameter-length ratio of 1, this comparison is based on results for cylinders of 1 in. diam. and 1 in. length. In general:

$$\Delta w = \pi C p x_0^2 = 2\pi^2 C f x_0^2$$

where the damping coefficient C is equal to $C_2 \frac{A}{l}$. Term C_2 can be obtained from Figure 8 as $C_2 = \frac{0.94 + 3.6\epsilon_s}{f^{0.83}}$

$$\Delta w = 2\pi^2(0.94 + 3.6\epsilon_s) f^{0.17} \frac{A}{l} x_0^2 \qquad (9)$$

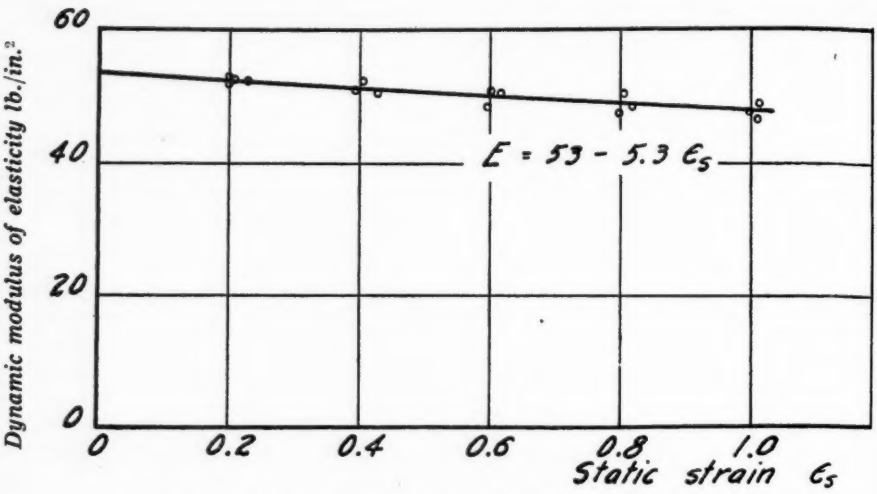


FIG. 19.—Effect of static strain on dynamic modulus of elasticity for shear specimens.

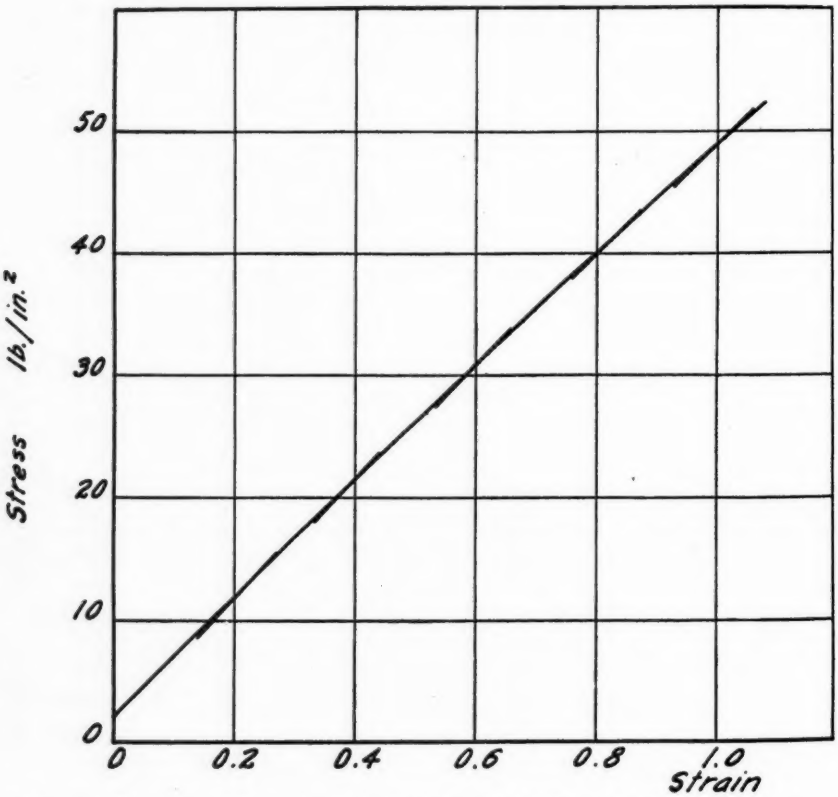


FIG. 20.—Comparison of dynamic modulus of elasticity with static modulus for shear specimens.

The total energy is:

$$W = \frac{1}{2} k x_0^2$$

For one cylinder:

$$k = \frac{EA}{l}$$

From Figure 11:

$$E = 240 + 590\epsilon_s$$

so:

$$w = \frac{1}{2} (240 + 590\epsilon_s) \frac{A}{l} x_0^2$$

Then:

$$\frac{\Delta w}{w} = 4\pi^2 \left(\frac{0.94 + 3.6\epsilon_s}{240 + 590\epsilon_s} \right) f^{0.17} \tag{10}$$

Equations (9) and (10) are in agreement with the first three conclusions of Roelig[4], *i.e.*, those in regard to the roles of dynamic load or amplitude, static load, and frequency in affecting the damping. In regard to the effect of volume, Equation (9) may be rewritten as:

$$\Delta w = \frac{2\pi^3}{4} (0.94 + 3.6\epsilon_s) f^{0.17} x_0^2 l$$

since the diameter is equal to the length. Term Δw varies directly as the length and so increases with volume. Equation (10) shows that $\frac{\Delta w}{w}$ is unaffected by changing the volume.

Equation (9) does not agree with the conclusion of Williams[5]. The energy lost in 1 cycle of stress increases with the frequency.

Results for the dynamic modulus of elasticity agree with the conclusion of Kosten[2] that the dynamic modulus is not affected by change of frequency.

CONCLUSIONS

The following conclusions apply to rubber of the stock tested when bonded to steel:

1. For cylinders in compression and specimens in shear, the damping can be expressed in terms of a velocity coefficient. The damping decreases with increase of frequency; it increases with increase of static strain.

2. The dynamic modulus of elasticity is slightly larger than the static modulus and is not affected by change of frequency. It increases with increase of static strain for the cylinders and decreases for the shear specimens.

3. For cylinders in compression, both damping and modulus of elasticity are dependent upon the ratio of diameter to length.

ACKNOWLEDGMENTS

The writer takes this opportunity to express his thanks to Prof. J. Ormondroyd, at whose suggestion and under whose direction the project was undertaken.

The specimens used were furnished by the United States Rubber Company. C. M. Sloman and F. L. Yost were especially helpful in this connection.

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FRICTIONAL PROPERTIES OF RUBBER*

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INTRODUCTION

The coefficients of friction of soft vulcanized rubber compounds have been studied by numerous investigators. The data reported for many of the investigations previous to March, 1934, have been collected and tabulated by Dawson and Porritt[1]. Most of the studies of the frictional properties of rubber deal with particular kinds of rubber goods, such as tires, power-transmission belts, soles and flooring, and water-lubricated bearings. In such studies the experimental conditions are those under which the products are commonly used. For example, the motion between the friction surfaces for tires or belts is a combination of rolling and sliding. Foreign materials, many of which act as lubricants, are nearly always present between the surfaces. Often, sliding is accompanied by vibration of the rubber, as in the case of the skidding of tires, where the vibration is distinctly audible.

In the present investigation, which is a part of a more general investigation on the abrasive wear of rubber, the specimens and tracks were prepared in the laboratory. This procedure makes it possible to employ a relatively wide range of experimental conditions and to exercise control over the composition and the surface of the specimens. No attempt was made to determine the skidding resistance of tires; instead the study was limited to the frictional characteristics of clean, soft rubber compounds, particularly those of the type used in tire treads, when sliding on clean smooth tracks. The effects of the presence of certain types of lubricants were briefly studied so that the results might be compared with those for relatively clean surfaces. Conditions of slide under which the specimens vibrate or chatter were not studied, except to note that the average force required to pull the specimen decreased considerably when chattering began. Because of chattering of the specimens, the maximum speeds for which friction was studied were limited to 10 cm. per sec. Also, because of difficulties experienced in preventing the specimens from buckling or otherwise deforming greatly, the maximum normal pressures between the specimens and the tracks were limited to 40 lbs. per sq. in. for most of the work.

EXPERIMENTAL PROCEDURE

Since this investigation was begun several years ago and then was discontinued for nearly two years before it was again resumed, the experimental procedure and data are presented in two parts. The first part was more in the nature of an exploratory investigation, consisting of brief studies of a relatively large variety of experimental conditions. The second part was a more detailed study of a rather limited field. Different samples, different apparatus, and different experimental techniques were employed in these two parts of the investigation, but the results are similar in many respects and lead to the same general conclusions.

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1. Earlier Experiments

APPARATUS AND PROCEDURE

The rubber specimens for most of this work were in the form of three circular disks, which were cemented to one surface of a rectangular metal plate in such a way that they shared equally the weight of the plate and the additional load. The disks were $\frac{1}{16}$ inch thick, and the diameters for different sets ranged from $\frac{5}{16}$ to $\frac{1}{2}$ inch. For some of the work, the rubber disks were replaced with steel, and the track was cut from the rubber to be studied. In some of the tests the metal plate and disks were towed along the friction track by means of a cord wound on a drum. A motor and reduction gear served to rotate the drum, and a spring scale in the tow line served to measure the frictional force. In other tests a circular friction track about 2 feet in diameter was rotated at the desired speed by means of the motor, and the specimens were held at rest by the tow line and spring scale.

RUBBER COMPOUNDS INVESTIGATED

The compositions of the rubber compounds used in the specimens are given in Table I. One is a typical pure-gum compound; the other is the standard

Table I

Composition of Rubber Compounds

[The standard abrasion and pure-gum compounds were press-vulcanized 60 and 30 minutes, respectively, at 142° C]

Ingredients	Rubber compounds	
	Standard abrasion	Pure-gum
	Parts by weight	*Parts by weight*
Rubber (smoked sheet)	100	100
Sulfur	3.5	3
Zinc oxide	20	5
Stearic acid	2	1
Di-*o*-tolylguanidine	1.25	...
Mercaptobenzothiazole (Captax)	...	1
Phenyl-β-naphthylamine	1	...
Channel black (Micronex)	30	...
Total	157.75	110

abrasion compound described in the Federal Specification for Rubber Goods, No. ZZ–R–601a. These compounds were selected for study because of their great difference in resistance to abrasion and to determine whether the coefficients were characteristic of the filler or of the rubber. Since specimens made from the soft pure-gum compound distorted greatly under conditions of slide, the larger part of the study was made on the standard abrasion compound and on specimens cut from a rubber conveyor belt, the exact composition of which was not known.

RUBBER SLIDING ON TRACKS OF DIFFERENT DEGREES OF ROUGHNESS

Coefficients of friction of the standard abrasion compound sliding on steel and on different grades of abrasive materials are plotted against the logarithm of the sliding speed in Figure 1. The logarithmic scale is used for the speed in this and subsequent figures for convenience in showing the coefficients over

a large range of speeds. The smoothest track was steel polished with No. 0 polishing paper. Various grades of abrasive papers, fixed on a rigid base, served as rough tracks. Figure 1 shows that, for every track, the coefficient

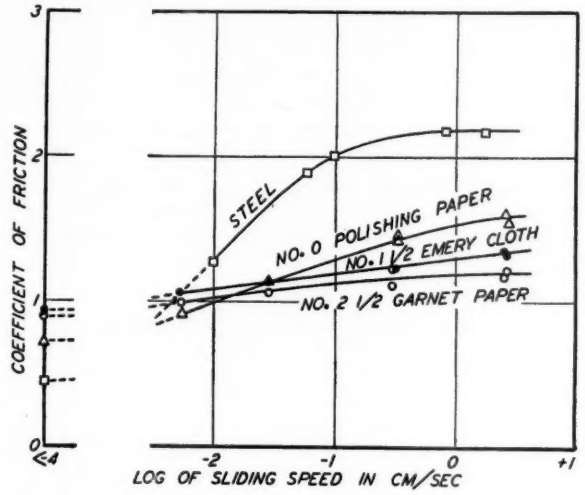

FIG. 1.—Coefficient of friction of rubber sliding at different speeds on surfaces of varying degrees of roughness.

The composition of the rubber is that given for the standard abrasion compound in Table I.

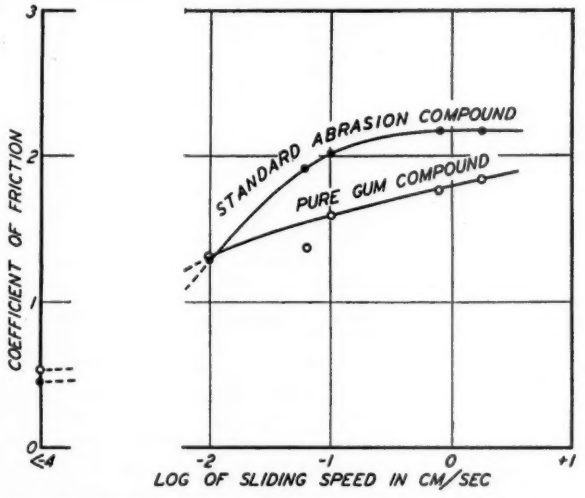

FIG. 2.—Comparison of the coefficients of friction of the two rubber compounds described in Table I when sliding at different speeds on a steel track.

The data for the standard abrasion compound are those shown for the steel track in Figure 1.

of friction increased with the speed. At the higher speeds the smoother tracks yielded the greater coefficients; but for speeds approaching zero, the rough tracks yielded the greater coefficients. Each point represents the average of

several observations. Except for the steel track, the data for the different points in each curve, particularly where two points occur for one speed, were obtained at various times over a period of more than a year. The values shown for the lowest speed were obtained by observing the spring scale after stopping the motor. The specimens continued to move on the track under the action of the spring for some time after the motor was stopped. Readings were taken when the specimen had apparently stopped. The normal pressures between the specimens and the track were 25 to 30 lbs. per sq. inch.

Figure 2 shows coefficients of friction obtained with the pure-gum compound on the steel track. The values for the standard abrasion compound shown in Figure 1 are also reproduced here for purposes of comparison. For these two compounds the increases of the coefficients with speed are similar. At speeds approaching 10 cm. per sec. the values of the coefficients became equal; but since the specimens vibrated at these speeds, the values were not plotted.

STEEL SLIDING ON A RUBBER TRACK

For the study of steel sliding on rubber, the rubber disks were replaced by steel disks of about the same size. The track, which was circular in form, was cut from a rubber-covered conveyor belt. Portions of this belt showed a decided tendency to bloom. The curves in Figure 3 show, respectively,

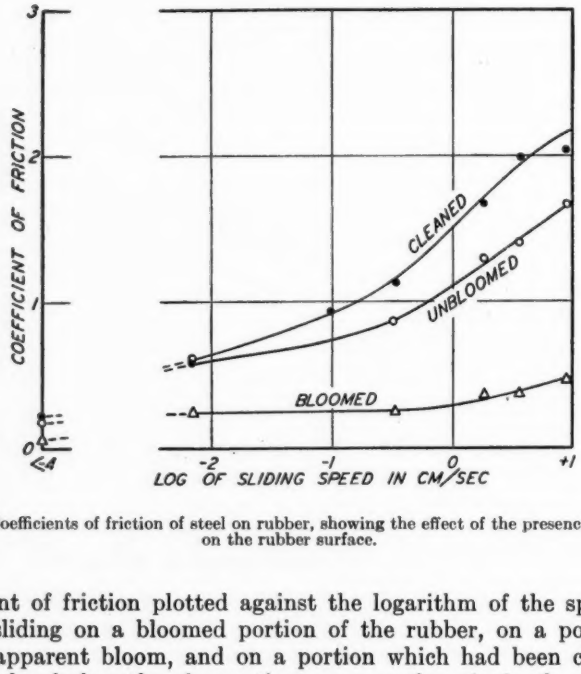

FIG. 3.—Coefficients of friction of steel on rubber, showing the effect of the presence of bloom on the rubber surface.

the coefficient of friction plotted against the logarithm of the speed for the steel disks sliding on a bloomed portion of the rubber, on a portion which showed no apparent bloom, and on a portion which had been cleaned with acetone the day before the observations were made. As in the previous experiments, the coefficients increased with speed in every case, although the presence of bloom sharply reduced the observed values.

EFFECTS OF CERTAIN LUBRICANTS

Since bloom or other materials which may be present on rubber compounds cause appreciable decreases in the observed coefficients of friction, a brief study was made of the effects of several materials which may have lubricating properties when present on the sliding surfaces. The materials selected were talc, spherulized kaolin[2], a thick soap solution, graphite, castor oil, and water. Talc is often used to facilitate sliding of one rubber article on another, as in the case of an inner tube in a tire. Spherulized kaolin might be expected to

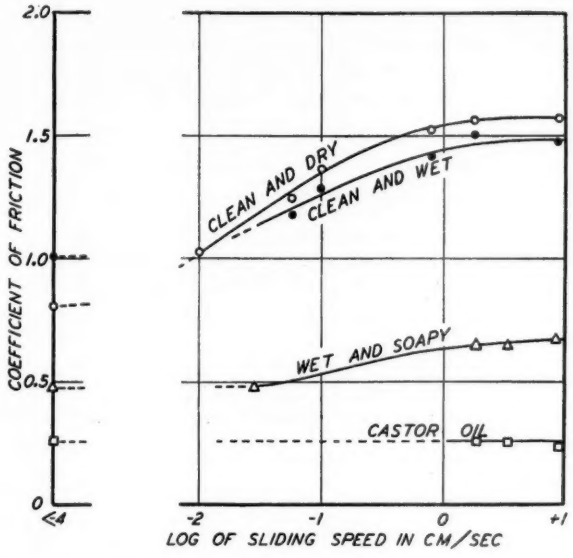

FIG. 4.—Coefficients of friction of rubber on rubber showing the effects of the presence of water, soap solution, and castor oil on the track.

possess lubricating properties because of its rounded particles. Soap, graphite, and castor oil are well known lubricants. Petroleum oils were not tried, since they cause swelling of the rubber. The effects of talc, spherulized kaolin, and graphite were studied for steel sliding on rubber and for rubber on rubber. The other substances were tried only for rubber on rubber.

In our experiments, talc and soap reduced the observed coefficients, but the increases in the coefficients with speed were still evident. Spherulized kaolin reduced the coefficients to a greater extent than talc did, but slight increases of the coefficients with speed persisted. The presence of graphite or castor oil on the sliding surfaces further reduced the coefficients, and the increases of the coefficients with speed disappeared completely.

For rubber sliding on rubber, wetting the surfaces with water caused a small decrease in the coefficients for the higher speeds, and a small increase as the speed approached zero. No general conclusions can be drawn from a single experiment of this kind. Observations reported later in this paper show that when rubber slides on glass, the presence of water causes a sharp decrease in the observed coefficients. Reports on the frictional characteristics of rubber sliding on glass and on roadway materials[3], of tires on roads[4], and of water-

lubricated bearings[5] show that the effect of water between the sliding surfaces depends markedly on the thickness of the water film and on other factors—such as the speed, the normal pressure, the nature and smoothness of the surfaces, and the presence of foreign materials in the water film.

ABRASION OF SPECIMENS ON A SMOOTH TRACK

In an attempt to determine whether any rubber was abraded from the specimens in sliding on a relatively smooth metal track, the specimens and plate to which they were cemented were weighed to 0.1 mg. before and after towing them several hours at about 3 cm. per sec. on the track. The procedure was repeated for increasing normal pressures between the specimens and track up to the point at which the specimens were torn apart by the frictional forces. No definite loss by abrasion could be detected for pressures up to 260 lbs. per sq. inch.

2. Later Experiments

COMPOUNDS INVESTIGATED

A large proportion of the measurements of coefficients of friction were carried out on specimens made from a channel black compound containing 49 parts of carbon black to 100 parts of crude rubber. The composition is shown in Table II. This compound is one of those used in an investigation

Table II

Composition of Rubber Compounds

[The specimens were press-vulcanized for 15 minutes at about 142° C]

Ingredients	Rubber compounds	
	Channel black	Clay
	Parts by weight	*Parts by weight*
Rubber (smoked sheet)	100	100
Sulfur	3	3
Zinc oxide	5	5
Stearic acid	2	2
Benzothiazyl disulfide (Altax)	1	1
Tetramethylthiuram disulfide (Tuads)	0.1	0.1
Phenyl-β-naphthylamine	1.5	1.5
Channel black (Micronex)	49	...
Clay (Dixie)	...	140
Total	161.6	252.6

of stress-strain properties at different rates of stretch[6]. Except for the omission of softeners or plasticizers which would facilitate manufacturing processes, it is a typical tire-tread compound.

Several specimens were also made of a compound in which the channel black was omitted. Because of distortions of the soft rubber under frictional forces, it was impossible to obtain satisfactory results with these specimens. Specimens were then made with a body of the channel-black compound and a thin layer of the soft compound on the sliding surface. These specimens chattered at the higher speeds, and at low speeds the frictional forces repeatedly increased to a maximum and dropped to a lower value.

Specimens were also made from a compound in which 70 parts of clay filler was substituted for the channel black. This amount of clay is equal in volume

to the amount of channel black which it replaced. These specimens jumped and chattered at speeds of 0.01 cm. per sec. or greater.

A number of satisfactory measurements of the coefficient of friction were obtained, however, on specimens made from a compound containing 140 parts of clay instead of channel black. This compound, referred to in Table II and elsewhere as the clay compound, possesses a hardness measured by resistance to indentation which is about equal to that of the channel-black compound.

APPARATUS AND PROCEDURE

(1) *General description.*—A schematic diagram of the two arrangements used in determining the coefficients of friction is shown in Figure 5. The horizontal track was suspended by four wires from points about 6 feet above it, and the specimen was pulled along the track at a constant speed by means

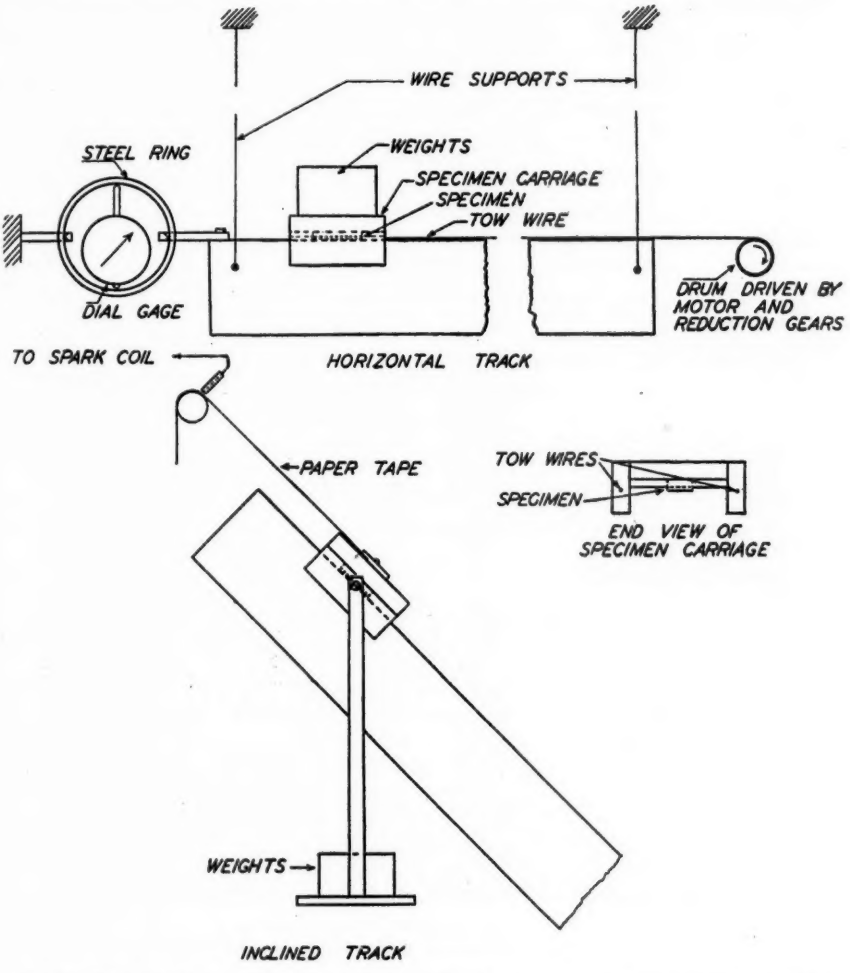

FIG. 5.—Schematic diagram of the two arrangements used in determining the coefficients of friction.

of a motor and reduction gears. The frictional force was determined by measuring the force required to hold the track at rest while the specimen was being moved. The coefficient of friction in this arrangement is the ratio of the measured force to the total weight on the specimen.

In the inclined-track arrangement, the specimen was allowed to slide down the track under the action of the combined weights of the specimen carriage and the additional load which was hung from it. In this case the frictional force remained constant, and the speed of slide was measured. The coefficient of friction is equal to the tangent of the angle made by the plane of the track and the horizontal.

(2) *Specimens.*—Attempts were made to use specimens which were cut from a sheet of rubber and fitted snugly into a recess in the under side of the carriage. As these specimens slid along the track, they became shorter and thicker, leaving an open space at the leading end of the recess, and finally they buckled. This excessive distortion was eliminated by vulcanizing the rubber stock to rectangular pieces of steel $\frac{1}{8}$ inch thick which fit into the recess. The rubber in these specimens was usually about $\frac{1}{16}$ inch thick, but increasing the thickness to $\frac{1}{4}$ inch produced no noticeable difference in the coefficients of friction. Most of the specimens had dimensions of either $\frac{5}{16}$ by $1\frac{1}{4}$ inch or $\frac{3}{4}$ by $1\frac{1}{2}$ inch. The direction of slide was parallel to the larger dimension, and the leading end was beveled to prevent the edge from rolling under.

The sliding surfaces of the specimens were of three types. The first, a smooth surface, was obtained by molding the rubber against plate glass. When these specimens were pressed against a glass surface, only part of their areas made actual contact with the glass. Interference fringes were observed around the boundaries of the contact areas, and considerable force was required to lift the specimens off the glass. The coefficients of friction observed differed greatly between individual specimens and between different observations on the same specimen. Examination of the specimens after they were allowed to slide on the track showed that only parts of their surfaces made contact and that the proportion of each specimen which made contact varied considerably between individual specimens.

To obtain more uniform conditions of contact and to get the pressure between the specimen and the track distributed more uniformly over the entire surface, specimens were made by molding the rubber against plate glass which had been roughened with an abrasive. Two degrees of roughness were obtained, one by roughening the glass with carborundum flour and the other by the use of 150-mesh carborundum. Much of the work reported here was done using these two types of specimens, which are referred to as specimens type *F*, and type 150, respectively. Photomicrographs of two specimens of type *F* and one of type 150 are shown in Figure 6. The specimen represented by the photomicrograph labeled *D* was obtained by cutting a piece of rubber from the tread of a used tire and cementing it to a rigid fiber back. The rubber was about $\frac{3}{32}$ inch thick, and care was taken to get the thickness nearly uniform. The tread surface shown here was used as the friction surface. Examination of Figure 6 shows that, except for a few relatively deep marks in the direction of the rotation of the tire, the roughness of this specimen is intermediate between specimens type 150 and type *F*. Only one such specimen was investigated.

(3) *Tracks for frictional measurements.*—Two kinds of friction tracks were used; one was a ground-steel surface and the other was plate glass. The steel

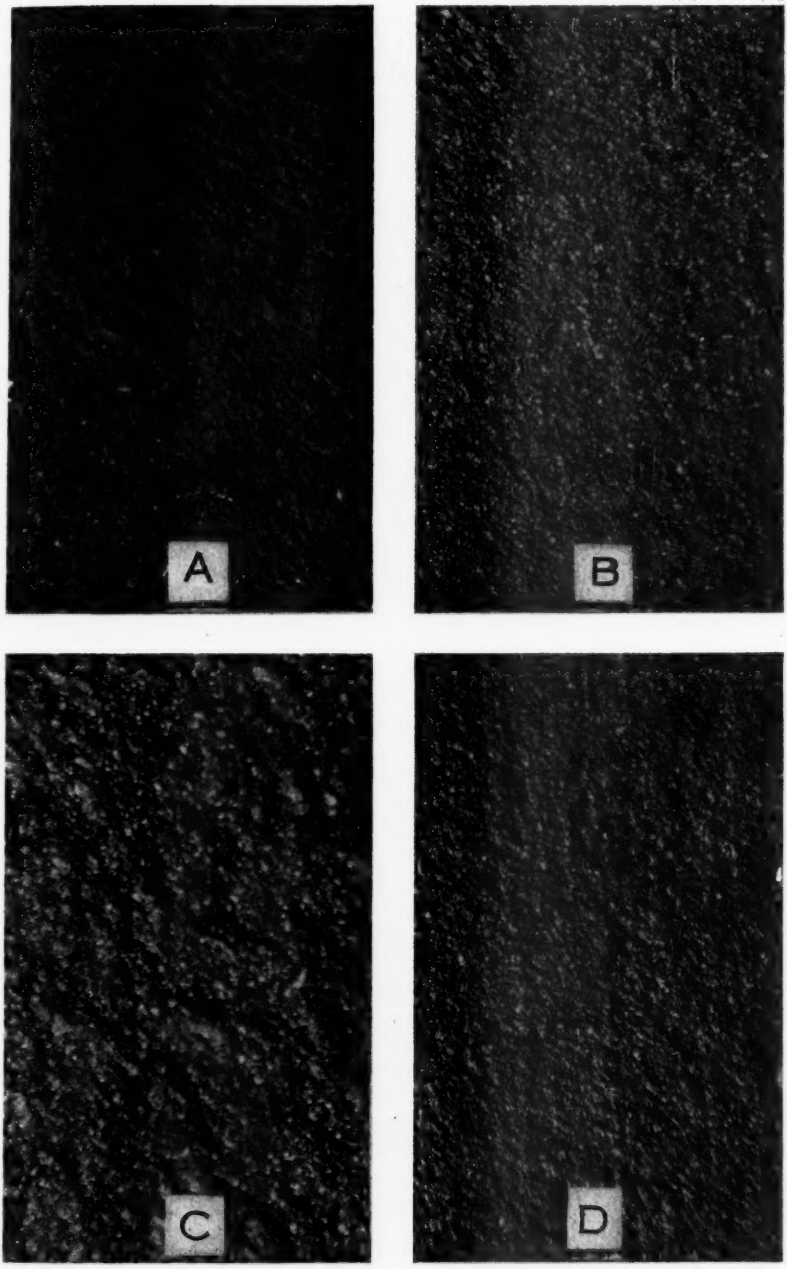

FIG. 6.—Photomicrographs of the sliding surfaces of the rubber specimens.
A and *B* are type *F*, *C* is type 150, and *D* is the specimen from a used-tire tread. Magnification 48×.

track was made from a piece of cold-rolled steel 1½ inches wide, 3 inches thick, and about 40 inches long. The friction surface was ground smooth with a a high-speed, fine-abrasive wheel. This surface was not polished and, consequently, was not as smooth as the glass track. Rusting of the steel, when not in use, was prevented by a coating of Alox rust preventive dissolved in Stoddard solvent. This coating was removed with gasoline followed by acetone prior to each use of the track.

The glass surface was obtained by clamping a strip of plate glass on top of the steel track. The glass was usually cleaned with soap and warm water followed by clean water, and usually dried with acetone. The use of acetone, though not necessary, was a quick and convenient means of drying the track. Occasionally the glass track was cleaned by immersing it for several hours in chromic acid. It was found that this occasional cleaning was sufficient to give reproducible results.

(4) *Mounting and loading of specimen.*—To keep the pressure between the specimen and the track uniform over the entire specimen surface, the carriage was so constructed that its center of gravity lay in the center of the surface of the specimen. When the carriage was used on the horizontal track, it was towed by means of two wires fastened equidistant from the specimen on either side and in the plane of the track. Any additional weights were placed centrally over the specimen on the top of the carriage. When the carriage was used on the inclined track, the additional weights were hung from pins placed in its sides equidistant from the specimen and in the plane of the track.

The loads applied to the specimens were such that the normal pressure on the sliding surfaces ranged from 2.5 to 15 lbs. per sq. in. for the large specimens and from 7.5 to 40 lbs. per sq. in. for the small ones. A large proportion of the work was done using 10 lbs. per sq. in. on the large specimens and 20 lbs. per sq. in. on the small ones.

(5) *Measurement of the frictional forces.*—The force to be measured in the horizontal-track arrangement was that required to keep the track from moving when the specimen was pulled. Since it was desired to measure this force with a minimum of displacement of the track, it was determined by measuring the distortion it produced when applied to a steel ring. The ring had an outside diameter of about 3.6 inches, and an inside diameter of about 3.3 inches, and was about 0.6 inch wide. It was fastened between the track and a fixed support, as shown in Figure 5, so that the force to be measured acted along the horizontal diameter. Distortion in the direction of the vertical diameter was measured by means of a sensitive dial gage graduated to ten-thousandths of an inch. The distortion shown by the gage rarely exceeded 0.008 inch (80 divisions), and calibration over this range showed that it was proportional to the force applied, the calibration factor being 305 grams per division.

(6) *Sliding speeds.*—The speeds on the horizontal track ranged from 0.0001 to 7 cm. per sec. Since observations became increasingly tedious as the speed was decreased, and since the coefficients at very low speeds were markedly affected by vibrations in the building, no attempt was made to extend the investigation on the horizontal track to speeds below this range. The maximum speeds, from 1 to 7 cm. per sec., were limited by jumping and chattering of the specimens on the track.

In the case of the inclined track, the speed was the quantity to be measured, while the forces acting on the specimen remained constant. As a convenient means of determining the speed, a paper tape was fastened to the specimen carriage and towed through a spark gap. Sparks produced at desired intervals

punctured the tape, making a permanent record of the position of the specimen as a function of time. The force required to pull the tape was negligible.

Usually the angle of incline was adjusted before the specimen was placed on the track; but when the equilibrium speed was over 0.01 cm. per sec., it was often necessary to allow the specimen to begin sliding with the track at a relatively low angle of incline, and to increase the angle as the speed decreased. Determinations of the speed were not made until the desired angle of incline was reached.

RESULTS

1. Changes in Frictional Forces at the Start of Slide

It was noted throughout the later experiments (Section II–2) that when a specimen was towed at constant speed on a horizontal track, the force of friction did not become constant until the specimen had moved several centimeters. Likewise, a specimen sliding down an inclined track moved several centimeters before it attained a constant equilibrium speed. Figure 7 shows the results of a study of these changes for typical specimens of type 150 and type *F* when sliding on a glass track. For the horizontal track the points on the graphs refer to readings of the force of friction which were taken at predetermined intervals of time. Care was taken at the start of slide to allow all the slack and stretch in the apparatus to be taken up before observations were begun. For the low speeds, readings were not taken until the specimen was allowed to move about half of a millimeter. In the case of the inclined track the position of the specimen was recorded at various intervals of time, and the average speed for each interval was plotted.

These changes in the frictional characteristics of the specimens at the start of slide were first thought to be due to nonuniformities in the friction track, but this explanation was ruled out by the fact that the phenomenon occurred on any portion of the track and on all the glass tracks which were used in the tests. Also, when the specimen was stopped during its slide and was started again, it repeated the changes which were observed at the beginning of the test and approached the same equilibrium conditions of slide. Furthermore, similar results were observed for specimens sliding on the steel track.

It appears that these changes of frictional properties at the start of slide are transitions from static conditions of contact between the friction surfaces to dynamic conditions, and are regarded as such in the more detailed discussions which follow, but it is not clear why the effect should extend over such a large distance of slide.

2. Coefficient of Static Friction

If the curves in Figure 7 (*A* and *B*) are extended back, one would expect them to intersect the zero ordinate at a point which corresponds to the coefficient of static friction. This point appears to lie somewhere between the values 1.2 and 1.5 for the specimen type 150 and between 1.5 and 2.0 for type *F*. Accordingly, if the specimens are placed on the inclined glass track, the maximum angle of repose should be between $\tan^{-1} 1.2$ and $\tan^{-1} 1.5$ for the specimen type 150 and between $\tan^{-1} 1.5$ and $\tan^{-1} 2.0$ for type *F*. It was found that the specimen type 150 always started sliding when the angle of incline was $\tan^{-1} 1.3$ or greater, seldom started when the angle was $\tan^{-1} 1.2$, and never started for angles appreciably less than $\tan^{-1} 1.2$. The maximum angle of repose for the specimen type *F* was similarly about $\tan^{-1} 1.6$.

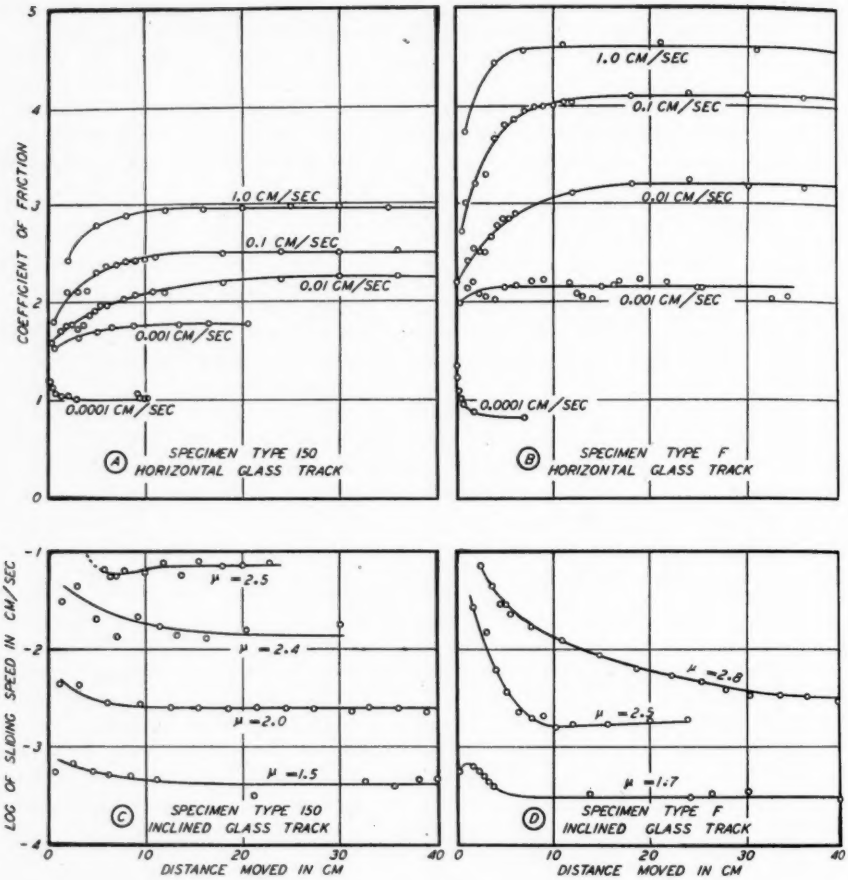

FIG. 7.—Changes in frictional properties of rubber at the start of slide.

Results are shown for two types of surfaces on horizontal and inclined glass tracks. μ is the tangent of the angle of incline, and is equal to the coefficient of friction.

3. COEFFICIENT OF DYNAMIC FRICTION

If one regards the changes of the frictional forces during the first several centimeters of slide on the horizontal track as transitions from static to dynamic conditions, the relatively constant coefficient finally reached is the coefficient of dynamic friction for that particular speed. Likewise the nearly constant speed which is attained after the first several centimeters of motion down the inclined track represents the equilibrium speed for that particular angle of incline.

The data from the equilibrium conditions shown in Figure 7 have been plotted in Figure 8 to show the relation between the coefficient of dynamic friction and the speed, and to show the correlation between tests made on the horizontal track and those made on the inclined track. This graph indicates that the coefficients obtained by use of the horizontal and inclined tracks are in agreement, that the coefficients of friction for both specimens increase as

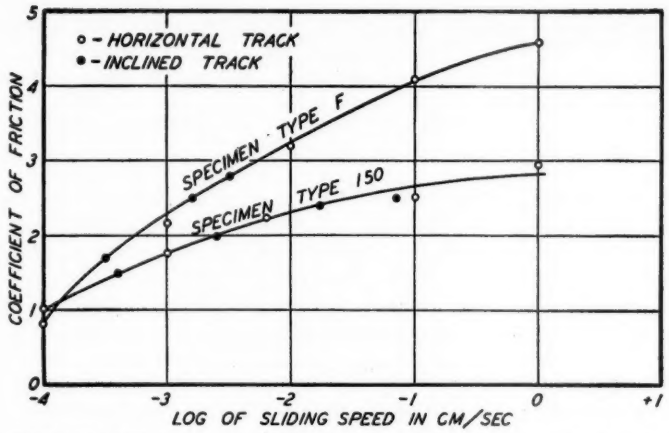

FIG. 8.—Coefficients of friction of channel-black rubber sliding at different speeds on a glass track. The data were taken from the equilibrium conditions of slide in Figure 7 and show the correlation between tests made on the horizontal and inclined tracks.

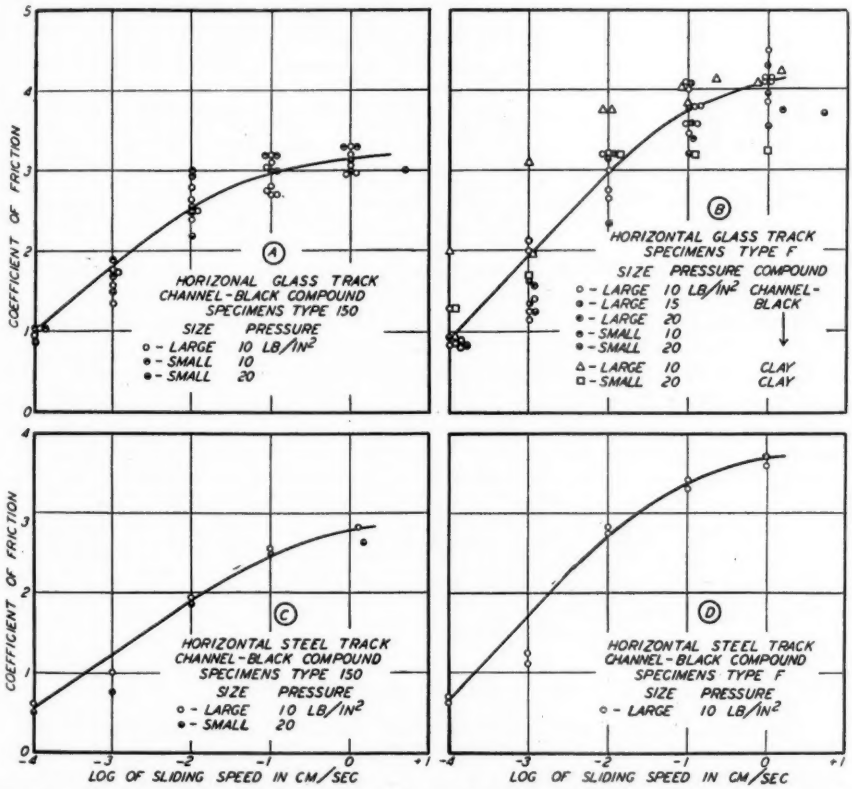

FIG. 9.—Comparison between the coefficients of friction of channel-black specimens type 150 and type *F* when sliding on glass and on steel tracks.

The individual graphs show variations in the coefficients for nominally identical specimens, for specimens of different sizes, and for various pressures. The dimensions of the large and small specimens are, respectively, ¾ by 1¼ inch and ¼ by 1¼ inch. Graph *B* also compares coefficients obtained for the channel-black and clay compounds.

the speeds increase, and that except for the lowest speed the coefficients for the surface with the finer texture, type *F*, are greater than those for type 150. These observations have been substantiated by results from several similar specimens (see Figure 9).

4. Relation Between Static and Dynamic Coefficients

It is evident from Figure 7 that the coefficients of dynamic friction for speeds of 10^{-3} cm. per sec. or more are greater than the coefficient of static friction, but it appears that, at a speed of 10^{-4} cm. per sec., the dynamic coefficients are the smaller. This phenomenon leads one to believe that if a specimen were once sliding under nearly equilibrium conditions, it should continue to slide down a track which is inclined at an angle less than the angle of repose. Accordingly, a specimen of type 150, for which several determinations showed that the angle of repose was not less than $\tan^{-1}$ 1.2, was placed on the inclined glass track and allowed to slide about 2 hours with the angle of incline at $\tan^{-1}$ 1.3. The angle was then decreased by small amounts at intervals of from 1 to several hours until it reached a value of $\tan^{-1}$ 1.1, where it was left for nearly 3 days. During this time the specimen slid about 12 cm., with an average and nearly constant speed of slide of 4.8×10^{-5} cm. per sec. The angle was again decreased by small steps until a value of $\tan^{-1}$ 1.0 was reached. With the track at this angle the specimen slid continuously for about 9 days, moving 16.5 cm. at an average speed of 2.1×10^{-5} cm. per sec. Thus experiments with both horizontal and inclined tracks show that at very low speeds the coefficient of dynamic friction is less than the static coefficient.

5. Effects of Various Factors on the Coefficients of Dynamic Friction

The effects produced on the coefficients of dynamic friction by changes of several experimental conditions are shown in Figures 9, 10, and 11. Each experimental point in these figures represents the nearly constant coefficient attained after several centimeters of slide. The four graphs of data plotted in Figure 9 show principally comparisons between the coefficients of friction of channel-black specimens of type 150 and type *F*, when sliding at different speeds on glass and on steel. The individual graphs show the effects of changing other conditions, but these will be discussed under separate headings. Much of the work presented in this figure has been substantiated by experiments on inclined tracks; but to avoid further complications of the graphs, these data have been omitted. Figure 10 shows the coefficients of friction for one channel-black specimen of each of the two sizes, when sliding under different normal pressures at a speed of 0.1 cm. per sec. on glass. Figures 7 and 10 were obtained from specimens which were cleaned with acetone prior to each test, but Figure 11 shows the effect of omitting this precaution.

Sliding Speed

The data for coefficients of friction of rubber presented in Figures 8, 9, and 11 have been plotted as a function of the speed. In every case the coefficient increases with the speed. This increase becomes relatively more pronounced for smoother and for cleaner sliding surfaces. In most cases the rate of increase of the coefficient in respect to the speed becomes less for speeds over 0.1 cm. per sec.

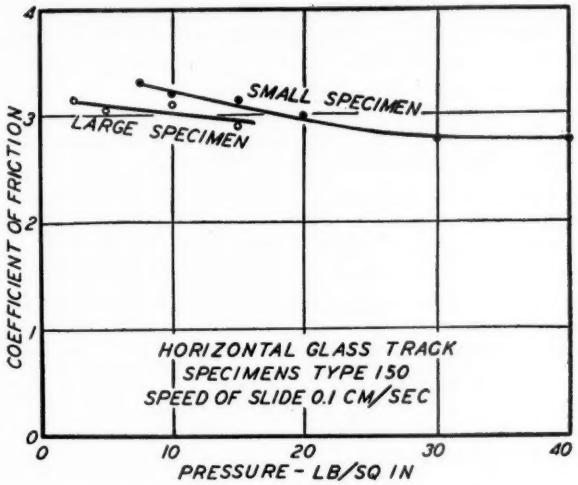

FIG. 10.—Coefficients of friction of rubber when sliding under different normal pressures on a glass track.

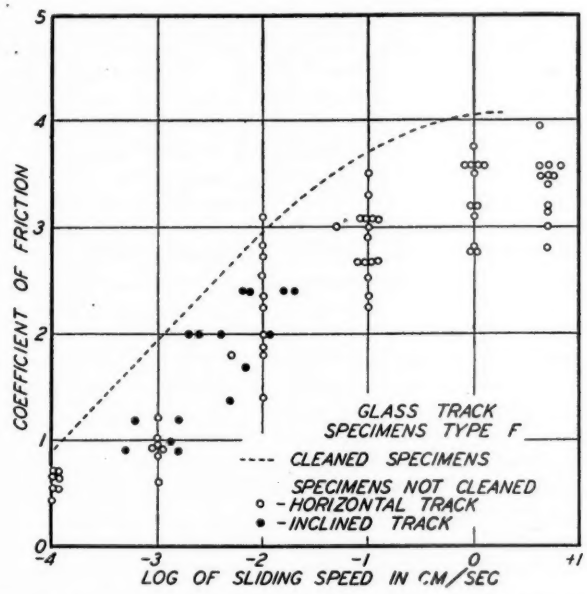

FIG. 11.—Coefficients of friction of rubber on glass, showing the effect of omitting the precaution of cleaning the surface of the specimens with acetone before the test.
The broken-line curve is the curve shown in Figure 9 (*B*).

Similar increases in the coefficients are also shown throughout the earlier experiments (Section II–1), where the conditions were quite different from those in the later experiments. The only cases in which the coefficients are independent of the speed are those for which the sliding surfaces were lubricated with graphite or castor oil.

Large decreases in the coefficients of all the specimens were observed when the speed reached a value at which the specimen began to vibrate or chatter. Chattering usually occurred between 5 and 10 cm. per sec. for the channel-black specimens of types *F* and 150. Specimens of softer compounds and those with smoother surfaces began to chatter at lower speeds.

ROUGHNESS OF THE SLIDING SURFACES

The data obtained in this investigation indicate that, except for very low speeds, less than 10^{-3} cm. per sec., the rougher the specimen surface or the rougher the friction track, the lower are the observed coefficients of friction.

The effect of the roughness of the specimen surface on the observed coefficients is suggested in part by the data shown in Figure 9, where, at any given speed except the lowest, the coefficients for specimens type *F* sliding on either glass or on steel are greater than the corresponding coefficients for specimens type 150. Additional confirmation of this effect is shown by a study of several specimens which had been molded against unroughened plate glass. The results obtained from these specimens are not shown here, because it was evident from the appearance of the sliding surfaces that only parts of them had actually come into contact with the track, and that the proportion of each specimen surface which made contact with the track varied considerably between individual specimens. However, it could be seen that, in spite of the great scattering of the data, the coefficients of the smooth specimens were appreciably higher, especially at intermediate speeds, than those for specimens type *F*. Furthermore, it was found that there were appreciable differences in the coefficients obtained for individual specimens of type *F*, Figure 9 (*B*). A closer examination of some of these specimens revealed that there were slight differences in the apparent roughness of these specimens, those showing the higher coefficients having a finer surface texture. For instance, in Figure 6, *A* and *B* are both photomicrographs of specimens type *F*, but the surface of *A* appears to be of a finer texture than that for *B*. Correspondingly, the coefficients obtained from *A* are appreciably higher.

The effect of the roughness of the track is illustrated by the data presented in Figure 1. In this work, the rubber specimens were drawn over various abrasive tracks, and, except for the lowest speed, the smaller the abrasive particles the higher were the coefficients obtained. Further evidence, though not conclusive in itself, is shown by Figure 9, where the coefficients for rubber on steel were found to be slightly less than the coefficients for corresponding specimens at the same speeds on glass. This difference might be due to differences in the nature of the materials, but it seems more likely to be due to the relative smoothness of the surfaces of the tracks, the glass track being somewhat smoother than the steel.

SURFACE AREA AND NORMAL PRESSURE

There seems to be no relationship between the coefficients and the specimen sizes. The data in Figure 9 show that differences between nominally identical specimens are of the same order as the differences between specimens of the two sizes employed. Figure 10 shows that the coefficients decrease only slightly with increasing pressure. In this figure the coefficients are plotted as a function of the normal pressure for one channel-black specimen of each of the two sizes when sliding on glass at a speed of 0.1 cm. per sec. The range of pressures investigated, 2.5 to 40 lbs. per sq. in., was determined by limitations of the apparatus.

VIBRATION OF THE APPARATUS

The values shown in Figure 9 (*C* and *D*) for the coefficients of friction at the speed of 10^{-3} cm. per sec. seem to be somewhat lower than would be expected from the values at the other speeds. A comparison of these coefficients with the results obtained from the inclined track also showed some discrepancy. It was found that the motor was causing vibration in the apparatus at this speed. When this vibration was eliminated, the observed coefficients became somewhat higher and in better agreement with those obtained from the inclined track. The values shown in Figures 7 and 8, and part of those shown in Figure 9 (*A* and *B*) were obtained after the vibration had been eliminated.

Further indications of the effect of vibration on the observed coefficients of friction is shown by the data for the lowest speeds plotted in Figure 7 (*A* and *C*). In the case of the horizontal track, Figure 7 (*A*), the seventh point represents an observation taken early in the morning, before general activity in the building began. The value of this coefficient is higher than those observed later in the day and during the previous day. Likewise, the seventh point for the inclined track, Figure 7 (*C*) represents the average speed during the night. This point is well below the other points, all of which represent speeds during the two days. Observations such as these have been made repeatedly.

COMPOSITION OF THE RUBBER COMPOUND

The frictional properties of a rubber compound seem to depend more on the rubber matrix than on the compounding ingredients or fillers. Since cleaned specimens of very soft rubber compounds show a strong tendency to chatter or vibrate on the tracks, even at relatively low speeds, only a limited amount of work was done with such compounds. Observations were made of the clay compound described in Table II, and data for three specimens of this compound were plotted in Figure 9 (*B*) for the purpose of comparing them with the data on channel-black specimens which had similar sliding surfaces. The surfaces of the specimens of both compounds were produced by molding them against plate glass which had been roughened with carborundum flour. The size of the clay specimens was the same as for the larger channel-black specimens, and the normal pressure was 10 lbs. per sq. in. The values of the coefficients of the clay specimens are rather widely scattered, but, for any one specimen, the general changes in the coefficients in respect to speed are quite similar to those obtained for the channel-black specimens.

A specimen taken from the tread of a used tire also showed frictional properties similar to those obtained from the prepared channel-black specimens. The surface of this specimen, shown in Figure 6 (*D*), had some rather high and low regions, but the general surface texture seemed to be not far different from some of the prepared specimens. Because the cement bond between the rubber and the rigid back of this specimen was not so strong as the bond between the rubber and the steel on the other specimens, the pressure was limited to about 6 lbs. per sq. in. The values of the coefficients of dynamic friction obtained on the horizontal glass track for this specimen, after cleaning it with acetone, were 1.3, 1.7, 2.1, 2.4, 3.0, and 3.4, respectively, for speeds of 0.0001, 0.001, 0.01, 0.1, 1.0, and 5 cm. per sec. These values are in approximate agreement with those given in Figure 9 (*A*) for specimens of type 150. The coefficients observed before cleaning ranged from 0.7 at 0.01 cm. per sec. to 1.1 at 1.0 cm. per sec. The frictional forces for the clean specimen showed

the usual increase in value during the first several centimeters of slide at speeds over 0.001 cm. per sec. and a decrease in value during the first several millimeters of slide at 0.0001 cm. per sec. Chattering of the specimen occurred during part of the sliding at speeds of 1 and 5 cm. per sec.

Another comparison between coefficients of friction of two widely differing compounds is shown in Figure 2. Because of differences in the experimental procedures, the actual values of the coefficients in this figure cannot be compared to those obtained in the later experiments (Section II–2), but it can be seen that the coefficients for these two compounds do not differ greatly over the range of speeds investigated.

CLEANING THE SPECIMENS

The specimens which were used for obtaining the data shown in Figures 7 to 10 were cleaned with acetone before each test. This procedure made possible more uniform results than could be obtained otherwise, and the actual values observed for the coefficients were not greatly different from those obtained when the specimens were tested immediately after removing them from the molds. Cleaning the specimens also permitted using them repeatedly with no observable change in frictional properties, whereas uncleaned specimens showed progressively lower coefficients as blooming progressed. Consequently, by cleaning the specimens it was possible to determine the equilibrium coefficients of dynamic friction of the same specimen for various conditions of slide (different speeds, normal pressure, horizontal and inclined tracks, etc.) instead of using a new specimen for each test and introducing unavoidable differences in surface roughness.

As an illustration of the effects of omitting the precaution of cleaning specimens, a number of coefficients of dynamic friction of uncleaned specimens are plotted as a function of the logarithm of the speed in Figure 11. The specimens for this work were left in the mold about two days after vulcanizing, and were placed on the friction apparatus as soon after removing them from the mold as possible. This procedure kept the specimens relatively clean and free from bloom, though probably not entirely so. As a means of comparing these values with those obtained from specimens which were cleaned with acetone, the curve from Figure 9 (*B*) is shown as a broken line. The data for both graphs were obtained from specimens with the same type of surface, namely type *F*. Figure 11 shows that the values of the coefficients of the uncleaned specimens scatter rather widely, but approach the values of the cleaned specimens as an upper limit. Similar observations have been made for specimens type 150.

MOISTURE

Although the relative humidities in the laboratory ranged from 10 to 80 per cent during the investigation of the coefficients of friction of rubber on steel and rubber on glass, there was no observable correlation between the coefficients observed and the relative humidity. In the case of rubber sliding on glass, the presence of visible water on the track or the specimen resulted in a sharp decrease in the coefficients observed. When the track was submerged in water, the values of the coefficients decreased to about 4 or 5 per cent of the values obtained for dry surfaces. Coefficients obtained after wetting the track and the specimen with water and allowing it to evaporate until all the visible water disappeared were not observably different from coefficients

obtained after drying the surfaces with acetone. No attempts were made to remove adsorbed water from the glass surface.

The effects of water on the coefficient of friction of rubber on steel were not studied, because of the possibility of changes in the nature of the steel surface due to corrosion.

6. Summary of Results

The experimental results obtained from this investigation may be briefly summarized as follows:

1. Dynamic friction increases with speed up to a certain critical speed at which the specimens chatter. The dynamic friction is less than static friction only at speeds less than about 10^{-3} cm. per sec.
2. Clean rubber specimens slide several centimeters before the friction becomes constant.
3. Except for very low speeds, the rougher the surfaces the lower are the observed coefficients.
4. The coefficient of friction of a rubber compound seems to be dependent more on the rubber matrix than on the compounding ingredients and fillers.

DISCUSSION

The four generalizations listed in the foregoing summary of results are discussed in order here under separate headings.

1. Sliding Speed

The increase of friction with speed for speeds ranging from 10^{-4} to 10 cm. per sec. was evident throughout the investigation. At the lowest speeds the values of the coefficients were seldom much over unity and were usually somewhat less. For speeds greater than the order of about 10^{-3} cm. per sec. the dynamic friction became greater than the static friction. At the highest speeds at which the specimens slid smoothly, the coefficients reached values ranging from somewhat over 2 to more than 4, depending on the cleanness and smoothness of the sliding surfaces. The limiting speed of smooth sliding seemed to be determined by the properties of the specimen, being nearly 10 cm. per sec. for the channel-black compound and less for softer compounds. The effect of the geometry of the specimen on this limiting speed was not studied, although there was no observable difference between the two sizes of specimens employed in the investigation.

CHANGE OF FRICTION WITH SPEED

Observations of coefficients of static friction which were less than dynamic coefficients and observations of dynamic friction which increased with speed have been reported at various times for rubber and for other materials. However, the reports do not include observations of such high values for the coefficients as have been found in the present investigation on rubber. That the static friction for rubber was less than dynamic friction was reported by James[7] in 1924 and by Derieux[8] in 1934 for sections of tires sliding on various surfaces. Derieux reported also that the friction increases with speed. Ariano[9] found that when a rubber belt was allowed to slip over a pulley, the coefficient of friction increased with the speed of slip. In an investigation of the frictional properties of small rubber blocks sliding on wet and on dry roadway materials,

Papenhuyzen[3] also showed coefficients of friction which increased with the speed.

A large proportion of the investigations on the frictional properties of rubber has dealt with the skidding of tires on roads. In many of the earlier investigations the tires were dragged on the road and the forces for starting motion and for maintaining it at some constant speed were used in determining, respectively, the coefficients of static and dynamic friction. Sliding speeds of less than 3 miles per hour (about 135 cm. per sec.) were seldom studied. It can be seen that if the coefficient increases sharply with speed and reaches a maximum value at a speed much lower than the one investigated, this maximum coefficient would be reached before the observer was aware that the specimen was moving and, consequently, would appear to the observer to be the coefficient of static friction. Thus one may readily account for the many observations of static coefficients which were greater than the dynamic coefficients. In more recent investigations[10] the coefficients were determined for various amounts of slip as the tire rolls along the road. In general, when braking forces or accelerating forces are applied, the tires begin to slip, so that the speed of rotation is not equal to the speed of a free-rolling wheel.

When a braking force is applied to the wheel, the amount of this slippage increases with the force until the wheel locks and slides. Moyer[4] showed that at 20 miles per hour on wet concrete, the coefficients of friction increased sharply with increasing percentage of slip, reaching a maximum value when the slip reached about 18 per cent of the vehicle velocity. The coefficient of friction reached 90 per cent of its maximum value at about 5-per cent slip. A slip of 5 per cent at 20 miles per hour corresponds to a sliding speed of 45 cm. per sec. The coefficients decreased as the slip increased above 18 per cent. Schmid[11] showed similar results for various types of roads by means of autographic recording of the braking force and the angular speed of the wheel. At 4 kilometers per hour (about 2.5 miles per hour) the coefficient of friction rose sharply with increasing slip up to 10 per cent of the speed of the vehicle, and then rose less rapidly as the slip increased to about 20 per cent. Beyond 20-per cent slippage the wheel often locked and the coefficient decreased. Because of the tendency for the wheel to lock, difficulty was encountered in determining coefficients for slippages above the point at which the coefficient reached a maximum value. Similar increases of friction with increasing slip have been obtained for various types of roads at the National Physical Laboratory[12].

VIBRATIONS

It is well known that when rubber slides on a solid surface, as in the case of a tire on the road, a distinctly audible vibration often occurs. In most of the investigations on frictional properties of tires, or of other rubber products, such vibrations seem not to have been given much attention. The coefficient of friction is usually regarded as the ratio of the average towing force to the load, irrespective of the condition of slide. Papenhuyzen[3], however, does study such vibrations for rubber sliding on glass and for rubber sliding on roadway materials. Employing an apparatus in which one end of a cylindrical rubber specimen was held coaxially against the face of a rotating disk of glass or of roadway material, he found that vibrations occurred at a critical speed which was greater for the roadway material than for glass. Below this critical speed, sliding was smooth, that is, no vibration occurred. Examination of the vibratory motion at speeds immediately above the critical speed by means of motion

pictures showed that the cycle of vibration consisted of two parts, one in which the specimen was distorted and the other in which the specimen "broke free"[13] and quickly receded to a position of much less distortion. The time required for the specimen to reach its maximum distortion depended on the speed of the disk and the amount the specimen slipped during the time of the distortion. This slippage was small, but observable. The time of relaxation depended largely on the physical characteristics of the specimen.

Vibrations of this type are known as mechanical relaxation oscillations[14]. Analogous oscillations occur in certain electric circuits. Mechanical relaxation oscillations are observed in oscillating systems of small inertia, where the restoring force increases with the displacement. An extensive study of such oscillations has been made of the bowed violin string[15]. Oscillations of this type have been explained[16] as being due to a decrease in friction with increasing speed. The decrease in friction with increasing speed was not actually observed in the present investigation, but Figures 1, 2, 4, and 9 indicate that the friction approached a maximum at the speed at which chattering occurred. Thus, it is reasonable to suppose that the chatter was accompanied by a decrease in friction beyond this maximum and that the chattering was a manifestation of relaxation oscillations.

Mechanical relaxation oscillations have been observed in materials other than rubber, metals in particular, but only with apparatus which possesses certain dynamical properties. Kaidanovsky and Haykin[16] studied such oscillations of a lubricated cylindrical journal bearing and stated that, to obtain such oscillations, it was necessary that the dynamic friction decrease with speed. Haykin, Lissovsky, and Solomonsky[17] describe these experiments in English and account for the "stick-slip" phenomenon of Bowden and Leben[18], in which no lubricant was employed, as a manifestation of such oscillations. Extensive studies of mechanical relaxation oscillations for both lubricated and unlubricated metals have been recently reported by Morgan, Muskat, and Reed[19].

In a theoretical discussion of relaxation oscillations, Blok[20] points out that these oscillations are not necessarily audible, but that they may be either subsonic or ultrasonic, depending on the characteristics of the sliding system. He also shows that, for certain materials and under certain conditions, the amplitude of the vibrations may be very small, and he calls such oscillations "microvibrations".

2. Changes in Friction at the Start of Slide

It was shown in Figure 7 that, when a rubber specimen was towed on the friction track, the coefficient of friction changed during the first several centimeters of slide. These changes were apparently from a value, which may be regarded as the static coefficient, to a constant equilibrium value, which may be regarded as the coefficient of dynamic friction for that particular speed. For speeds greater than 10^{-3} cm. per sec. the coefficient increased from the initial value, and at speeds appreciably less than 10^{-3} cm. per sec. the coefficient decreased. This change in friction may be connected with the peculiar properties of thin films of water which may be present on the sliding surfaces. Derjaguin[21] has shown that thin films of water possess definite and measurable shear moduli and yield points. A further confirmation of the rigid properties of thin films of water has recently been reported by Eversole and Lahr[22]. An explanation of this property of the film supposes the existence of long chains of oriented water molecules extending from the solid surfaces into the interior

of the liquid. Papenhuyzen[3] supposes that the presence of such films on the sliding surfaces would account for values of friction which are higher than would otherwise be observed. In addition he supposes that orientation of the molecules and formation of chains would be enhanced by sliding of the surfaces, and that a certain time would be required for the formation of these chains. This idea is similar to that presented by Hardy and Doubleday[23] in explanation of the time required to reach equilibrium conditions of slide when certain oils are employed as boundary lubricants.

If one were to apply this idea to the data in Figure 7, one would arrive at a chain formation time of about 10 seconds for the speed of 1.0 cm. per sec., 100 seconds of 0.1 cm. per sec., and so on. At the speed of 10^{-4} cm. per sec., however, the chains do not seem to be formed, since the friction decreases to its equilibrium value.

3. Roughness of the Sliding Surfaces

That the higher coefficients are obtained with the smoother surfaces is in contradiction to frictional characteristics for many commonly observed sliding conditions. This conclusion, however, applies only to the range of speeds from about 10^{-3} cm. per sec. to speeds at which the specimens vibrate. Below 10^{-3} cm. per sec. it appears that the rougher surfaces show the higher coefficients. It will be noted that the speed of about 10^{-3} cm. per sec. is also the critical speed above which the coefficients at the start of slide increase, and below which they decrease.

Since measurements of the area of contact could not be made without considerable difficulty, no attempt was made to correlate the various coefficients with the actual contact area of the specimens. The finer surfaces present more points of contact than do the coarser surfaces, but this fact does not indicate the relative contact areas.

4. Composition of the Rubber Compound

Since rubber is the external phase in a rubber-filler system, one might expect that the filler should not greatly affect the frictional properties of the compound. Changes in other physical properties, modulus of rigidity for example, would necessarily affect the critical speed at which vibrations in the specimen occur. The inclusion of waxes, oils, or other materials in the compound which come to the surface would be likely to affect the coefficients greatly, and were avoided as far as possible in this work. Cleaning the specimens prevented lubrication due to blooming of the ingredients which were employed.

SUMMARY

Laboratory measurements of coefficients of friction of soft rubber compounds were made by towing specimens on horizontal tracks and by allowing them to slide down inclined tracks. The specimens were prepared by attaching the rubber to a metal backing and molding it against glass surfaces having different degrees of roughness. The coefficients increase markedly with speed, ranging from about 1 at 10^{-4} cm. per sec. to more than 4 at 5 cm. per sec. The occurrence of vibrations prevented observations at higher speeds. Static friction is greater than dynamic friction for speeds appreciably less than 10^{-3} cm. per sec. and less than dynamic friction for greater speeds. The coefficients

decrease slightly with increasing pressures and are independent of the size of the specimen. Except at very low speeds the smoother surfaces yield the higher coefficients. Materials such as talc or bloom on the sliding surfaces cause large decreases in the coefficients.

Attention is called to the dependence of the coefficients of friction on the speed, which is shown in several previous investigations on rubber and other materials.

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RISE OF TEMPERATURE ON FAST STRETCHING OF SYNTHETICS AND NATURAL RUBBERS *

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That rubber warms when stretched rapidly, and cools down when released, is one of the earliest recognized peculiar characteristics of this material. It was observed first in 1805 by Gough[1]. Sometime later, Page[2] rediscovered the same effect. Many years later, Joule[3] independently observed this effect and made some quantitative measurements of the temperature rise due to fast stretching. Not much work was done along these lines until after about 1924, when it became of interest to find the heat given off by rubber during stretching. This heat could be measured in three different ways: (1) direct calorimetric measurement of the heat exchange when rubber is stretched isothermally; (2) determination of the temperature rise during adiabatic stretching, and (3) measurement of the change in heat content between stretched and unstretched rubber on melting or going into solution.

The first method has not yet been utilized successfully. The second was used by Joule[3], Chauveau[4], Williams[5], Ariano[6], Boone and Newman[7] and Ornstein, Wouda, and Eymers[8]; this is the method to be treated in this work. A number of authors have worked on the third method; there has been wide disagreement between the results obtained.

Sensory observation, *i.e.*, stretching rubber rapidly or, better, holding it stretched and then letting it retract quickly and touching it to the lips, shows that the maximum change in temperature should be greater than 10° C. Surprisingly, experiments reported in the literature[9] thus far give only about one-third of the expected value. Aside from the fact that an obvious discrepancy exists, this phenomenon is of great interest in tire construction.

EXPERIMENTAL PROCEDURE

A schematic diagram of the apparatus employed is shown in Figure 1. The ends of the rubber sample were sandwiched between pieces of scrap rubber to prevent the clamps from cutting the sample. The elongation was regulated by adjusting the distance the weight was allowed to fall. The ratchet was used to hold the weight before extension and to hold the rubber extended before retraction.

The rubber samples used were dumbbell-shaped, with a center section 0.25 inch wide and about 1.5 inches long. Two such samples were clamped as a sandwich and given a half twist to ensure good heat contact between the sample and the thermocouple. Thus the samples clamped the thermocouple increasingly tighter as greater elongations were attained. It was ascertained that this twist had no influence on the results of the experiment. The thermocouple was placed between the samples at the midpoint. The elongation was determined by measuring with a cathetometer the distance between marks on the center section of the strip. The thermocouple was made of copper and constantan wire 0.004 inch in diameter.

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The galvanometer was of the double suspension type, having a period of the order of 0.1 second and a sensitivity of about 10^{-7} ampere per mm. at a scale distance of 1 meter. The speed of this instrument was more than ample for our purposes. In combination with the light thermocouple, this galvanometer made it possible to read a temperature change within at least 0.2 second.

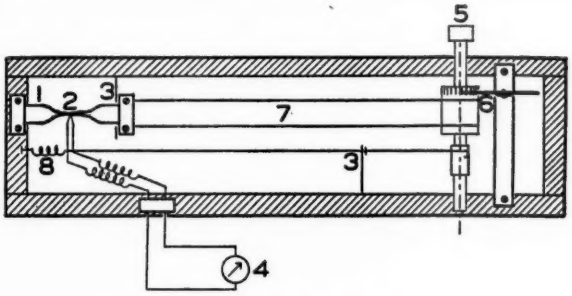


FIG. 1.—Diagram of apparatus.

1. Rubber sample
2. Thermocouple
3. Stops used during retraction
4. Galvanometer
5. Pulley system
6. Ratchet
7. Cables
8. Weak spring

In general, the temperature change on extension was different from that on retraction. Thus, a curve was run for both. In the graphs, the solid curve is for extension, and the corresponding points are indicated by crosses. The dashed curve and the circles are for retraction. The procedure for taking data for a curve was as follows. The weight was released and the temperature change noted. After the elongation had been recorded, the sample was released and the temperature change again noted. This was done on the same sample for the whole curve, beginning at small elongations and working up to larger elongations until the sample broke.

TEMPERATURE EFFECTS

The first sample was an undercured latex stock. The temperature effect (Figure 2) is reversible up to about 230 per cent. Above this point the cooling effect on retraction is larger than the heating on extension. The change in slope of the curves around 250 per cent marks the beginning of crystallization. The maximum elongation attained before the sample broke was only about 550 per cent, and the temperature changes seem to be such that the two curves would cross if higher elongations were attainable.

The next sample was also an undercured latex stock, and the curve (Figure 3) is similar to that of Figure 2 except that higher elongations were obtained. It is to be noted that the curves do cross. The highest temperature change for this run was 13.7° C at 674 per cent elongation.

An accelerated gum stock gave a similar curve (Figure 4).

An 8 per cent sulfur unaccelerated stock gave a different type of curve (Figure 5). There is no sudden change of slope, and the temperature changes are comparatively small. This implies that there is no crystallization. The curves are very close together, which suggests that the process is nearly reversible. Also the curve for retraction lies beneath that for extension.

Figure 6 was obtained for Hycar-OR. This also shows no crystallization. This substance was very plastic, and allowed an elongation of only about

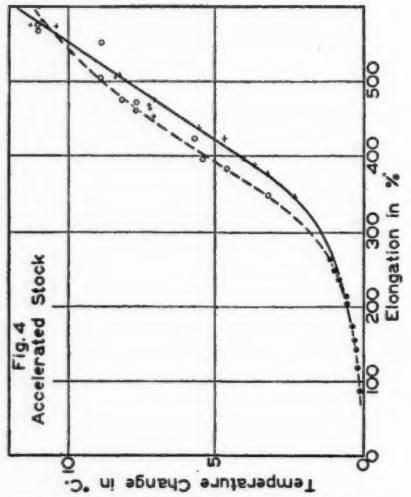


Fig.4
Accelerated Stock
Temperature Change in °C.
Elongation in %
0
5
10
100
200
300
400
500

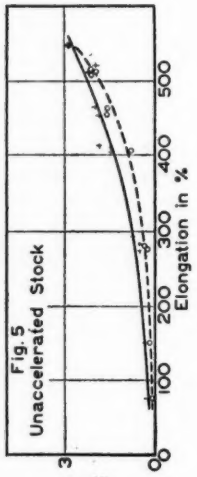
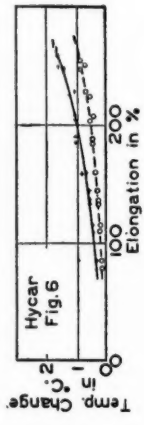


Fig.5
Unaccelerated Stock
Temp. Change in °C.
Elongation in %
0
3
100
200
300
400
500


Hycar
Fig.6
Temp. Change in °C.
Elongation in %
0
1
2
100
200

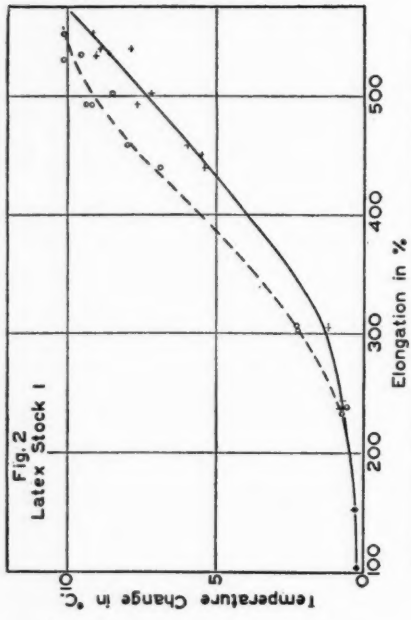


Fig.2
Latex Stock 1
Temperature Change in °C.
Elongation in %
0
5
10
100
200
300
400
500

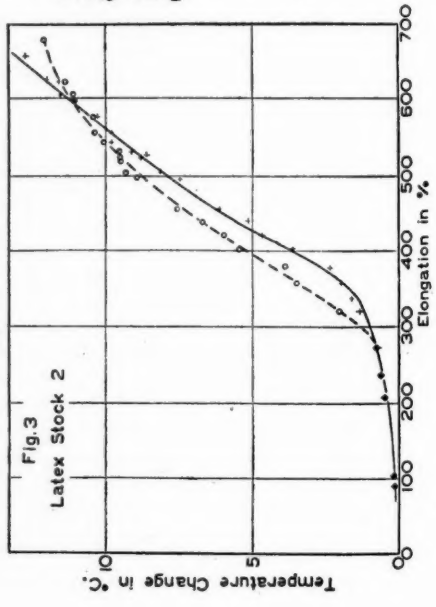


Fig.3
Latex Stock 2
Temperature Change in °C.
Elongation in %
0
5
10
100
200
300
400
500
600
700

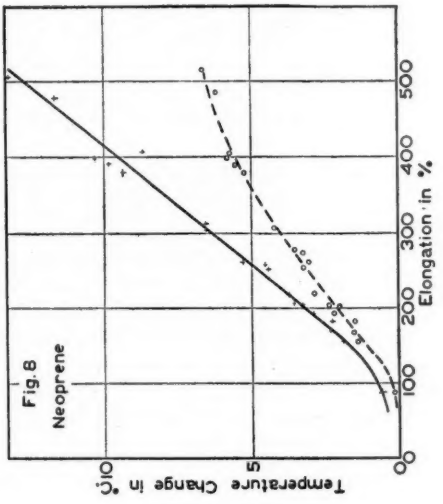


Fig. 8
Neoprene
Temperature Change in °C.
0
5
10
0
100
200
300
400
500
Elongation in %

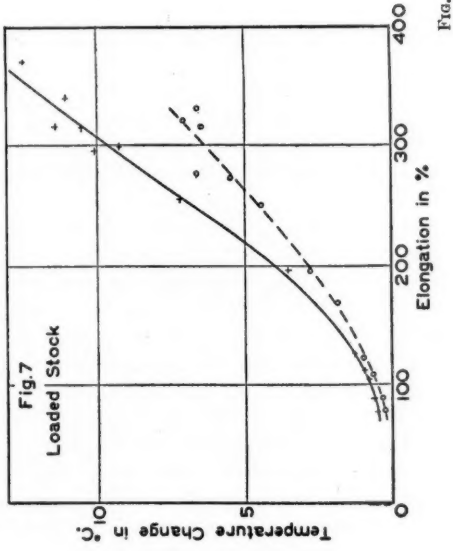


Fig. 7
Loaded Stock
Temperature Change in °C.
0
5
10
0
100
200
300
400
Elongation in %

FIG. 2.

250 per cent before breaking. Here the retraction curve is definitely lower than the extension curve.

The next sample was a heavily loaded stock. Figure 7 shows a sharp change in slope at the small elongation of 100 per cent. This is probably due largely to internal friction rather than crystallization. The retraction temperature change is only slightly more than one-half the extension temperature change. Since this means a large heating but small cooling, it is seen that, for a complete extension-retraction cycle, a comparatively large net temperature rise should result. This is of special interest, as tire treads are made from stocks of this type.

The last sample tested was a loaded Neoprene stock, and the curve (Figure 8) is similar to the loaded rubber curve. This sample was much tougher than any of the other samples.

A few variations were tried to obtain a general picture. A study was made of the variation in the retraction temperature change as a function of the time the rubber was kept stretched before retraction. For times of 1 to 5 minutes the variation was negligible, but for a 2-hour stretch an increase of 10 per cent in the retraction temperature change was noted. If a sample was greatly elongated on the first stretch, it gave a temperature change nearly 30 per cent greater than the curve would indicate. Thus, for rubber of the second type mentioned a temperature rise of 14.7° C was observed at 571 per cent on the first stretch.

EXTENSION–RETRACTION RESULTS

In general, accelerated stocks appear to give a higher temperature change on retraction than on extension for the range 300 to 500 per cent. Below this range the extension and retraction curves are nearly the same. The temperature changes for extension of loaded stocks were the greatest of any of the types investigated, but the plastic flow was such as to prevent extreme elongations. For the loaded stocks the retraction curve was much lower than the extension curve.

For the accelerated stocks the curves took a sharp upward trend near 300 per cent. This is assumed to be due to the beginning of crystallization, because x-ray analysis shows that the rubber does begin to form into a crystalline state at about this point. A large portion of the heat observed above this point is probably latent heat of fusion. It is of interest to note that the temperature response of the rubber was immediate for elongations less than 300 per cent, but above this there was a lag of the temperature behind the elongations. This lag amounted to as much as 5 seconds for high elongations, and could not possibly be due to slowness in the galvanometer or thermocouple response. The heat contact of the thermocouple to the rubber was best at high elongations because of the twist in the sample. This implies that some process which takes a small amount of time must have been going on in the rubber during elongation. Williams[5] too found this time lag, but attributed most of it to the slow response of his set-up, and so he extrapolated back to get his temperature changes. A time lag of 1.2 seconds after stretching, before a photographic fiber diagram was obtained with x-rays, was reported by Acken, Singer, and Davey[10]. However, Hauser and Mark[11], as a result of visual observations with the aid of a fluorescent screen, found no detectable time lag.

CONCLUSIONS

This investigation covered more types of rubber and rubberlike synthetics than were studied by previous investigators. From the results it seems apparent that at least a part of the disagreement between previous workers on this subject is due to the different types of rubber employed. It is also important to note that the temperature changes observed were of the order predicted by sensory observation.

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ACTION OF ORGANIC ACCELERATORS IN BUNA-S *

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Buna-S is an unsaturated polymer capable of undergoing vulcanization. This may be effected by the application of heat in the presence of sulfur. The process is accelerated by certain organic substances which are used widely for a similar purpose in natural rubber. Preliminary tests have indicated that most of them are applicable to Buna-S, and appear superior to any other chemicals yet investigated. This is fortunate in view of the present emergency, as plants for their manufacture already exist and the industry is familiar with their use.

In spite of superficially similar effects, more careful study has indicated that it is an oversimplification to assume various accelerators will produce identical effects in both polymers. A wide range of materials is now available to the industry, and the task of accurately evaluating all of them is complex. In addition, an indefinite number of combinations are theoretically possible. The present investigation was undertaken to determine what effect different chemical types of organic accelerators were likely to have on properties of fundamental importance.

COMPARISON OF BUNA-S AND NATURAL RUBBER

Properties of Vulcanized Compounds.—As a background, it is necessary to examine certain basic characteristics of the polymer under investigation to determine the relative magnitude of those properties likely to be modified by organic accelerators. In Table I, Buna-S and natural rubber are compared with this end in view. These data refer to tread-type compounds containing

TABLE I

COMPARISON OF BUNA-S AND NATURAL RUBBER IN TREAD-TYPE COMPOUNDS

Test	Buna-S	Natural Rubber	Reference
300% modulus (lbs. per sq. in.)	1200	1300	Fig. 1
Tensile strength (lbs. per sq. in.)	3300	4100	Fig. 1
Elongation (percentage)	500	600	Fig. 1
Accelerated aging (% change in tensile strength)			
96 hrs. in oxygen bomb at 70° C and 300 lbs. pressure	−14	−32	[1]
12 hrs. in air bomb at 125° C and 80 lbs. pressure	0	−82	[1]
Grasselli abrasion loss (cc. per h.p.-hr.)	70	200	[2]
Tear resistance by Crescent method (lbs. per in. thickness)	290	638	[3]
Max. temp. rise in Goodrich Flexometer (° F)	100	58	This lab.
Dynamic flexing in Goodyear machine (min. to failure)	21	130	[2]

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approximately 50 parts of carbon black and, for the most part, represent values reported in the literature.

It is evident that Buna-S is poorer in tear-resistance, heat buildup, and flexing, but superior in aging and resistance to abrasive wear. The ultimate tensile strength developed in a tread-type stock is lower than that in natural rubber, although the general character of the stress-strain curves are similar. The low tensile strength of unloaded Buna-S vulcanizates is recognized as a serious deficiency for certain applications and, for this reason, the present study will be confined to compounds containing appreciable loadings of carbon black; this type of stock is considered to be of the widest immediate interest.

The values in Table I for relative abrasion losses are undoubtedly wider than differences which are likely to be found under service conditions. It seems reasonable to conclude, however, from results already reported[4] that Buna-S treads may be expected to resist abrasive wear at least as well as, if not better than, natural rubber.

There have been conflicting reports regarding the ability of Buna-S to withstand dynamic flexing. Sebrell and Dinsmore reported values[2] based on laboratory data which would indicate it to be relatively inferior. Street and Ebert[1], on the other hand, found it to be better if the pigments were properly dispersed but stated that otherwise it was likely to be poorer.

In this laboratory, results from dynamic flexing tests on Buna-S have been extremely erratic for the number of flexures required until the first cracks appear. Thereafter, however, their rate of growth is extremely rapid and appears to be a reproducible phenomenon, which provides a basis for comparing the effect of accelerators.

The low tear-resistance of Buna-S may be a factor contributing to the rapid growth of cracks, once they appear. For convenience in evaluation and

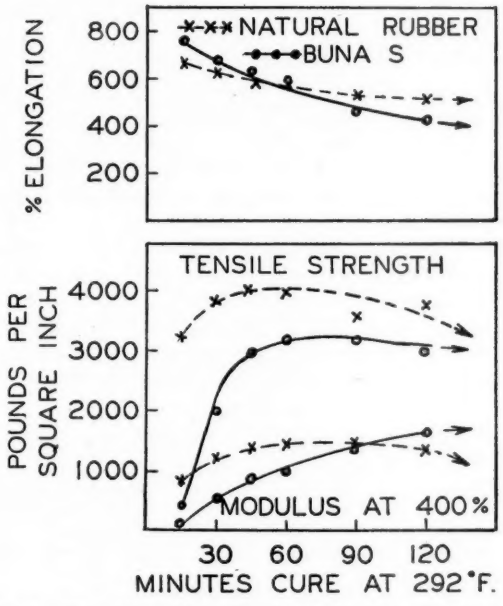

FIG. 1.—Comparison of Buna-S and natural rubber vulcanizates.

discussion, these two properties (growth of cracks on dynamic flexing and tear) will be referred to collectively as brittleness.

Rate of Cure.—The relative rates of cure exhibited by different accelerators are vitally important from the point of view of factory processing, and obviously must be considered on the same plane with properties produced in the finished vulcanizate. Figure 1 compares the curing rates of natural rubber and Buna-S in tread-type stocks, which are identical in every respect except for the basic polymer.

Under the above conditions natural rubber comes to its optimum cure in approximately 30 minutes, whereas Buna-S requires about 60 minutes. It also vulcanizes considerably more slowly at 227° to 239° F, which is an indication of greater processing safety.

These data show that, for practical purposes, Buna-S is slower curing than natural rubber; consequently it would appear advisable to investigate the possibility of overcoming this either by using higher ratios of accelerators or more active types, the limiting factors being processibility and adverse effects on quality in the vulcanizate.

The slower rate of cure at processing temperature is offset to some extent by a tendency of Buna-S to develop greater heat during mixing, calendering, and extruding operations. Evidence to date indicates, however, that the net effect will be in favor of Buna-S, which admits the possibility of using stronger curatives.

Reversion.—Figure 1 illustrates an additional fundamental difference between the basic polymers which is likely to influence the evaluation of accelerators. The modulus of Buna-S increases progressively with time of vulcanization, whereas that of natural rubber decreases after reaching a maximum value. This phenomenon in natural rubber is referred to as reversion, and is characteristic of long overcures. Buna-S does not revert in the manner characteristic of rubber, but tends rather to become progressively stiffer with prolonged curing.

A similar phenomenon is characteristic of Buna-S vulcanizates on accelerated aging. As will be seen later, the rate of stiffening has been found to be a more sensitive aging index than the change in tensile strength, which decreases at a relatively slow rate. This is in marked contrast to vulcanized natural rubber, which tends to go to a soft tacky condition during the early stages of aging, which is characterized by a decrease in modulus and tensile strength.

An examination of the interior of samples which have blown out in the Schopper detrition test exhibit these characteristics strikingly. Buna-S specimens appear hard and dry, whereas natural rubber is usually soft and tacky.

Summary of Comparison.—From published data[1,2,3] and from inspection of Figure 1, it may be assumed that, in general, those characteristics in Buna-S, compared with natural rubber, which are likely to affect the evaluation of accelerators may be summarized as follows:

Buna-S is equal or superior to natural rubber in:	Buna-S is likely to be inferior to natural rubber in:
Abrasion	Dynamic flex cracking
Aging	Heat build-up
Reversion on overcuring	Brittleness
Tendency to scorch during processing	Rate of vulcanization

This table may serve as a guide, therefore, in investigating the action of organic accelerators. Inasmuch as brittleness and heat build-up appear to be

major deficiencies in Buna-S, the effect of accelerators on these properties have been emphasized in the present investigation.

EXPERIMENTAL PROCEDURE

Buna-S is a new material in this nation, and procedures for testing it have not been standardized. Therefore the following remarks on techniques followed in this laboratory in the present study undoubtedly will be of interest.

It is well known that Buna-S requires substantial loadings of a reinforcing pigment to develop physical properties comparable to those of natural rubber; hence it is to be expected that thorough pigment dispersion is of prime importance. It follows, therefore, that differences in the relative degree of pigment dispersion are likely to influence results obtained when evaluating other compounding ingredients. Consequently it is necessary to maintain rigid control of processing procedures if reproducible results are to be achieved.

Processing.—The following principles in regard to mixing and curing were adhered to after a thorough study of various procedures. Compounds were mixed on an open mill with initial roll temperatures constant for each run. All batches were mixed according to a rigid time schedule; compounding ingredients were added in the same order and at the same rate each time. Specimens were vulcanized in a press as soon as possible after mixing; all cures were carried out at 292° F.

Physical Properties of Vulcanizates.—Modulus, tensile strength, and elongation at break were determined on a Scott machine according to A. S. T. M. procedures.

Heat Build-up and Hysteresis.—These characteristics were determined by the torsional hysteresis test[5], with a Goodrich Flexometer[6] operated at a load of 58.5 pounds and a stroke of 0.125 inch. The torsional hysteresis test was quicker to perform, but the Goodrich Flexometer appeared to be more sensitive.

Dynamic Flexing.—Ordinary dynamic flexing tests gave erratic results which were not reproducible. It was possible, however, to obtain consistent results by following the rate of growth of cracks which were present initially as nicks, one inch apart, in the groove of a standard bending moment flexing sample. Results are expressed as "brittleness" on a scale varying from 0 to 10. Actually this scale is based on the width of a crack in inches at the end of 50,000 flexures. Thus superior flexing or relatively low brittleness is characterized by a low rating, whereas 10 indicates complete failure. Admittedly this records only the rate of growth of a crack which already exists, and ignores the introduction period before its initial appearance. However, it describes an important property of Buna-S which is a factor in resistance to dynamic flexing and tear-resistance. A similar technique has been used in other laboratories[7] with satisfactory results.

Scorching Characteristics.—It has been standard practice in many laboratories to estimate scorching tendencies of natural rubber by the relative time required for incipient vulcanization in a press at 220° F. Buna-S compounds required several hours to show evidence of curing at this temperature. Consequently, the test was accelerated by increasing the temperature to 239° F. This change did not alter the relative ratings of several accelerators investigated.

Accelerated Aging Tests.—The usual tests were carried out in standard equipment. Buna-S compounds are much more resistant to accelerated aging than natural rubber. The increase in modulus or decrease in elongation on prolonged exposure to air at 212° F was found to be the most sensitive index.

Abrasion Tests.—Where run, laboratory tests showed no consistent differences between various accelerators; consequently no values are reported.

Test Formulas.—All data in the present investigation were obtained from a base compound of the following composition:

Buna-S	100
Carbon black	50
Fatty acid	2
Softener	5
Zinc oxide	5
Sulfur	Variable
Accelerator	Variable

The Buna-S was a copolymer of butadiene and styrene prepared by an emulsification process. The above compound was chosen as a type which is likely to be of wide immediate interest. Strictly speaking, all results reported here apply only to this compound and to the particular polymer utilized in this study.

EFFECT OF AMOUNT OF SULFUR

Compounds Containing 2 Parts of Sulfur.—Table II shows the effect on physical properties of varying amounts of mercaptobenzothiazole (MBT), cyclohexylbenzothiazyl sulfamine (sulfamine), and tetramethylthiuram monosulfide (TMTMS) in compounds containing 2 parts of sulfur. They were chosen as typical representative of the thiazole, sulfamine, and dithiocarbamate classes.

TABLE II

EFFECT ON PHYSICAL PROPERTIES OF VARYING AMOUNTS OF ACCELERATORS

Parts of accelerator per 100 parts polymer	Minutes to optimum cure at 292° F	Lbs. per sq. in.		Elongation (%)
		Modulus at 300%	Tensile strength	
		Mercaptobenzothiazole		
0	600	600	2900	580
0.25	180	675	3000	580
0.50	120	800	3200	560
0.75	90	910	3475	540
1.00	60	1000	3600	530
1.50	40	1150	3600	480
2.00	20	1200	3500	430
		Cyclohexylbenzothiazyl sulfamine		
0	600	600	2900	580
0.75	60	900	3500	560
0.85	50	1010	3560	550
1.00	40	1100	3500	545
1.50	30	1400	2300	350
2.00	20	1650	1900	325
		Tetramethylthiuram monosulfide		
0	600	600	2900	580
0.200	60	720	3400	650
0.250	45	880	3500	645
0.275	35	900	3510	640
0.350	30	1000	3440	600
0.425	20	1140	3240	550
0.500	15	1480	2400	390
2.250	10	...	1600	250

Compounds were cured over a range of time at 292° F, but only those values which represent the maximum cure for each accelerator variation are reported. A blank containing no accelerator is included. The reduction in curing time resulting from the addition of small proportions of accelerator is striking evidence of their economic value in manufacturing operations. The data reported in Table II are shown graphically in Figure 2.

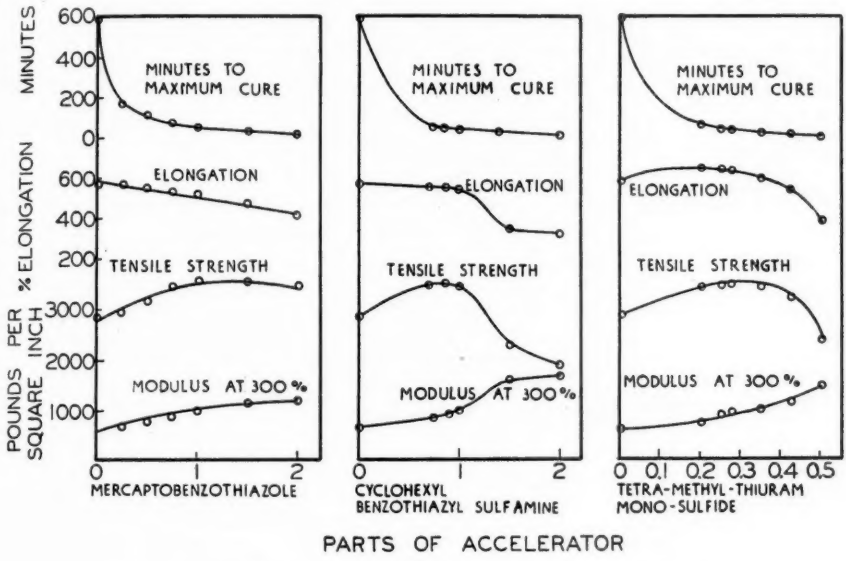

FIG. 2.—Effect of accelerator concentration on rate of cure and physical properties.

Increasing ratios of accelerator increase moduli and, in general, decrease breaking elongations. For each accelerator there is a specific concentration range in which maximum tensile strength is developed. As this range is exceeded, tensile strength becomes progressively lower, accompanied by a corresponding decrease in breaking elongation and increase in modulus.

This is not an unexpected result. The rapidity with which physical properties decrease when the optimum concentration of accelerator is exceeded, however, appears to place a limitation on decreasing curing times by resorting to excessive accelerator ratios. The data indicate that better physical properties are likely to result from using a more active type and staying within the limits of its optimum concentration.

The data show a more drastic decrease in physical properties for the higher concentrations of the sulfamine and TMTMS than for MBT, because the two former substances are stronger on an equal weight basis; it is believed that higher concentrations of the latter would result in a comparable falling-off of tensile strength.

Examination reveals no significant differences between the maximum tensile strengths developed by each accelerator at its optimum concentration. There does appear to be a distinct difference, however, in the modulus values between the MBT and TMTMS stocks. This relation is brought out in Figure 3,

where physical properties for two compounds accelerated with 1.5 per cent MBT and 0.35 per cent TMTMS, respectively, are plotted as a function of time of vulcanization.

The MBT compound comes to its optimum properties more gradually and, being more persistent, eventually develops a higher modulus which approaches an asymptote. The TMTMS compound, by contrast, rises to its maximum properties rather suddenly, starting later but coming to a full cure sooner. The modulus also appears to remain constant at a lower level once the maximum value has developed. The lower moduli are also reflected in higher breaking elongations throughout the curing range.

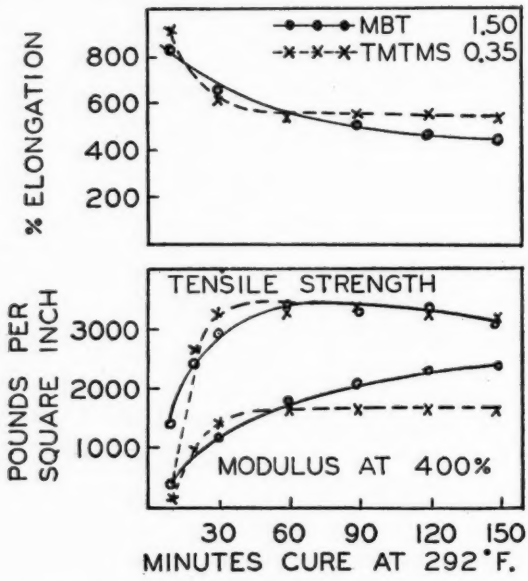

FIG. 3.—Comparative effects of mercaptobenzothiazole and tetramethylthiuram monosulfide on physical properties in Buna-S.

It is interesting to note that neither compound exhibits any tendency toward reversion, and both appear to have equally broad curing ranges. In fact, the nonpersistent quality exhibited by the TMTMS vulcanizate might be interpreted as evidence of a comparatively broader curing range. This is in sharp contrast to the performance of these two materials in natural rubber, in which dithiocarbamates usually exhibit narrow curing ranges in compounds containing normal sulfur ratios.

The foregoing comparison describes a pattern which all thiazoles and dithiocarbamates appear to follow in Buna-S. The former may be described as being more persistent and thus developing higher ultimate moduli and lower breaking elongations. The significance of these observations in relation to other properties will be discussed later.

The sulfamines and thiazolines follow patterns similar to the thiazoles in the development of physical properties as vulcanization progresses. The sulfamines lag somewhat during the early stages, and this is apparently reflected in greater processing safety. An outstanding feature of the thiazolines is their

tendency to develop higher moduli than any other single accelerator which has been investigated by this laboratory.

Table III lists the optimum ratios found for accelerators, judged by the development of maximum tensile strength. These data are reproduced to establish the relative activity of materials which are available commercially. Strictly speaking, the results are applicable only to the compound in which they were investigated. It is believed, however, that the same relative ratings should apply generally.

TABLE III

RELATIVE ACTIVITY OF ACCELERATORS IN BUNA-S CONTAINING 50 PARTS BY WEIGHT OF A REINFORCING CARBON BLACK AND 2 PARTS OF SULFUR

Accelerator	Optimum ratio	Minutes to full cure at 292° F	Minutes to incipient vulcanization at 239° F	Cure-burn ratio (minutes to cure divided by minutes to incipient vulcanization)
None	0	600	...	...
Thiazoles				
Mercaptobenzothiazole	1.5	40	40	1.00
Dibenzothiazyl disulfide	1.5	45	45	1.00
Zinc benzothiazyl sulfide	2.0	40	40	1.00
Methyleneaniline mercapto-benzothiazole	1.5	40	42	0.95
Sulfamine				
Cyclohexylbenzothiazyl sulfamine	1.0	40	60	0.66
Thiazoline				
2-Mercaptothiazoline	1.25	45	45	1.00
Dithiocarbamates				
Tetramethylthiuram disulfide	0.35	20	30	0.66
Tetramethylthiuram monosulfide	0.35	30	60	0.50
Zinc dimethyldithiocarbamate	0.40	20	20	1.00
Dinitrophenyl ester of dimethyldithiocarbamate	1.25	45	72	0.62
Aldehydeamine				
Butyraldehydeaniline	1.50	60	50	1.2
Guanidine				
Di-*o*-tolylguanidine	2.50	90	75	1.2

The above ratios are approximate, and vulcanization rates may be further adjusted by varying the concentration, within limits, of any particular accelerator. Care must be taken, however, not to overaccelerate, because of a deleterious effect on physical properties.

Some of the dithiocarbamates are more active than any members of any other group, and the monosulfide exhibits unusual safety, as shown by its extremely low cure-burn ratio. The zinc salt of dimethyldithiocarbamate is also very active but likely to be relatively more scorchy at processing temperatures.

The aldehydeamine and guanidine are comparatively weak, and exhibit unfavorable cure-burn ratios. The low pH of the carbon black in the batch is undoubtedly a factor contributing to their low order of activity. This should not preclude further consideration for them in nonblack compounds. In fact, there is evidence that some aldehydeamines may develop higher tensile strengths than other types in compounds loaded with zinc oxide or a fine particle size whiting. Because of their relative inactivity in the base compound under investigation, they will not be considered further in the present study.

Intermediate and Low Sulfur.—Table IV shows the physical properties resulting from various ratios of MBT and TMTMS in the presence of 1 per cent and 0.5 per cent of sulfur, respectively. The thiuram is more efficient than the thiazole at low sulfur ratios. The differences become progressively greater as the sulfur concentration decreases. It is also evident that Buna-S is still sensitive to excess accelerator ratios even at low sulfur levels.

TABLE IV

EFFECT OF INTERMEDIATE AND LOW SULFUR CONTENTS ON PHYSICAL PROPERTIES

Accelerator	Parts of accelerator per 100 parts polymer	Minutes to maximum cure at 292° F	Lbs. per sq. in.		Elongation (%)
			Modulus at 500%	Tensile strength	
		One part sulfur			
Mercaptobenzothiazole	1.5	60	1130	2600	800
	3.0	55	1400	2710	706
	4.5	50	1580	2570	713
Tetramethylthiuram monosulfide	0.25	30	880	1860	800
	0.50	30	1450	3040	710
	1.50	30	...	2500	450
		0.5 part sulfur			
Mercaptobenzothiazole	1.5	75	615	1400	890
	4.5	60	990	2220	800
Tetramethylthiuram monosulfide	0.35	60	600	1310	816
	2.0	30	1500	3200	700
	3.0	30	1550	2830	666

Vulcanization without Sulfur.—Vulcanization in the absence of sulfur may be effected by tetramethylthiuram disulfide. The process is analogous to the action of this compound in natural rubber. A tensile strength (Table V) in excess of 3000 pounds per square inch may be achieved by using a concentration of 3 parts per 100 parts of polymer; the time required for vulcanization at 292° F is approximately 30 minutes. The properties are similar to those obtained with 0.5 part sulfur and 2 parts tetramethylthiuram monosulfide (Table IV).

TABLE V

VULCANIZATION OF BUNA-S WITH TETRAMETHYLTHIURAM DISULFIDE WITHOUT SULFUR

Parts tetramethylthiuram disulfide	Minutes to cure at 292° F	Lbs. per sq. in.		Elongation (%)
		Modulus at 500%	Tensile strength	
3	15	1250	2680	733
	30	1750	3170	683
	60	1860	3180	670
	90	1930	3200	636
	120	1960	3000	620
5	15	...	2180	470
	30	...	2170	406
	60	...	2200	403
	90	...	2080	386
	120	...	1930	370

Concentrations of tetramethylthiuram disulfide in excess of 3 parts produce progressively lower tensiles, and exhibit the same trend typical of overacceleration in compounds containing 2 parts of sulfur.

EFFECT OF SULFUR-ACCELERATOR RATIO ON PHYSICAL PROPERTIES

The determination of physical properties at different sulfur contents is complicated by the ratio of accelerator present. This must be adjusted for each sulfur level; otherwise an unbalanced compound will result. Table VI

TABLE VI

VARIATION IN PHYSICAL PROPERTIES WITH SULFUR-ACCELERATOR RATIO

Sulfur	0.5	1.25	2.0	3.0
Accelerator	2.0	0.5	0.35	0.275
Tensile strength at optimum cure (lbs. per sq. in.)	3200	3180	3470	3190
Elongation at optimum cure (%)	750	720	600	540
Minutes to optimum cure at 292° F	30	30	30	30

shows the tensile strengths and elongations obtained at various sulfur levels for a series of balanced compounds accelerated with appropriate quantities of TMTMS.

These data show a sulfur content of approximately 2 parts to give the maximum tensile strength, although it is doubtful if these differences are real. As sulfur content is increased, curing range becomes progressively narrower, judged by the decrease in elongation at break over a range of cures. It is interesting to note that no significant change takes place in the time required to reach the maximum cure, judged by physical properties.

AGING

Effect of Accelerators.—Typical results obtained with a thiazole and two dithiocarbamates on accelerated aging in an oxygen bomb and an air oven at 212° F are recorded in Table VII. These data indicate that the dithio-

TABLE VII

EFFECT OF DIFFERENT ACCELERATORS ON AGING OF BUNA-S VULCANIZATES CONTAINING 2 PARTS OF SULFUR

Period of aging (hrs.)	% change in tensile strength			% change in elongation at break		
	Mercapto-benzothiazole (1.5)	Tetramethyl-thiuram monosulfide (0.27)	Tetramethyl-thiuram disulfide (0.35)	Mercapto-benzothiazole (1.5)	Tetramethyl-thiuram monosulfide (0.27)	Tetramethyl-thiuram disulfide (0.35)
Oxygen bomb at 70° C (158° F) and 300 pounds						
120	−22	−16	−11	−22	−16	−14
240	−24	−28	−26	−23	−24	−22
360	−27	−33	−28	−26	−31	−24
Air oven at 212° F						
48	−25	−15	−20	−41	−29	−31
96	−24	−16	−21	−48	−43	−43
144	−31	−29	−31	−53	−56	−56
192	−39	−32	−33	−58	−66	−61
240	−40	−43	−44	−66	−75	−74

carbamates resist aging somewhat better during the early stages, whereas the thiazole appears to overcome these differences during the longer aging periods. In either instance the variations are comparatively small, and it seems reasonable to assume that no appreciable differences exist between the two types.

The aging characteristics of all the accelerators listed in Table III were investigated, and no consistent or apparently significant differences were found. It is concluded that accelerators are not controlling in the aging of Buna-S

vulcanizates, and that for practical purposes this factor may be neglected when selecting suitable types.

Buna-S resists oxidation better than natural rubber, and the results obtained are in good agreement with those previously reported in the literature[1]. It has been observed, however, that undercured stocks do not resist oxidation well. Prolonged overcuring, on the other hand, does not appear to have an adverse effect.

Effect of Sulfur Concentration.—Compounds containing lower concentrations of sulfur age relatively better. The relation is comparable to the results observed[8] in natural rubber, although the variations are considerably smaller in magnitude.

HEAT BUILD-UP AND HYSTERESIS

Effect of Accelerators.—Figure 4 reveals the effect of cure and accelerator concentration on heat build-up. The results were obtained with a Goodrich Flexometer, and are expressed as the maximum temperature rise (ΔT) in ° F at equilibrium. All samples were brought to 100° F before starting the test. Samples were built up from pieces died out of tensile slabs.

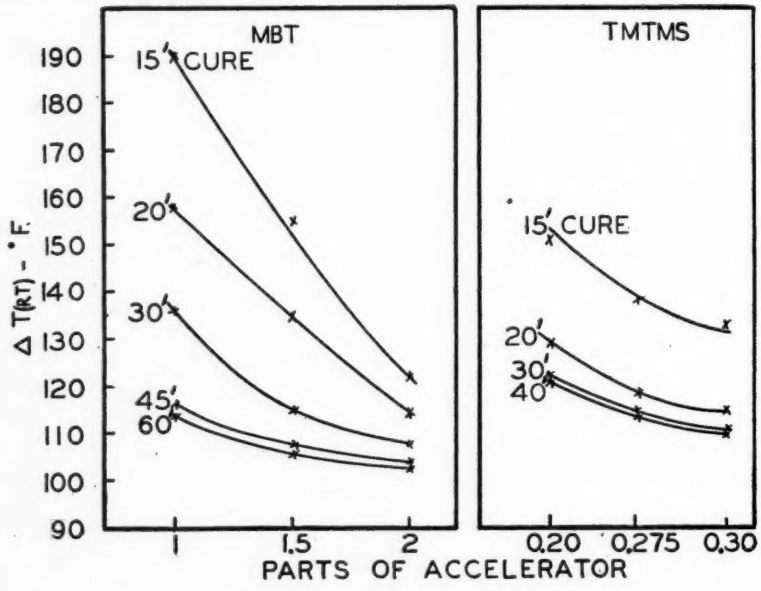

FIG. 4.—Effect of increasing amounts of accelerator and time of cure on heat build-up.

Figure 4 shows that ΔT decreases with progressive curing times, and reaches a practical minimum at a state of vulcanization which corresponds roughly to the one which gave maximum physical properties as indicated in Table III. It is also evident from Figure 4 that ΔT becomes progressively lower with increasing concentrations of accelerator. This would indicate that, other things being equal, a vulcanizate containing an excessive amount of accelerator would exhibit minimum heat build-up, although tensile properties would have declined in the manner characteristic of overaccelerated compounds as shown in Table II.

Effect of Sulfur Concentration.—Figure 5 shows the effect of sulfur on heat build-up characteristics, although these results are reported as torsional hysteresis. They are expressed as K, the logarithmic decrement. Essentially this is a measure of the rate of damping by a rubber specimen which has been deflected in a suspended position by the application of a torque. Lower values of K correspond to lower hysteresis. The tests were performed at 280° F, and

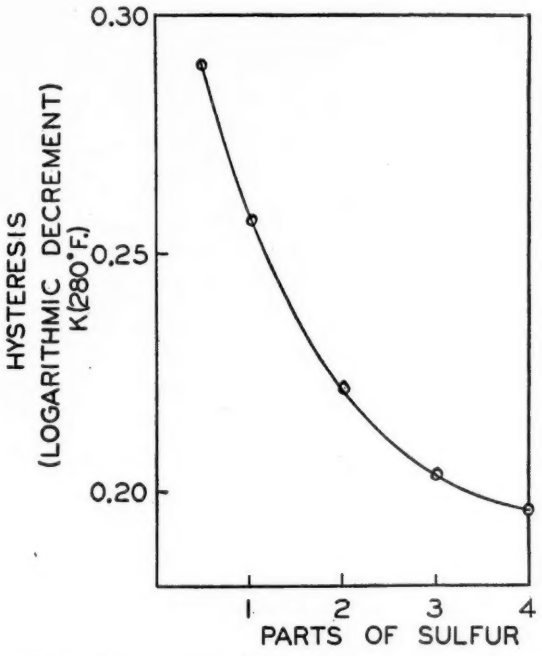

FIG. 5.—Effect of increasing amounts of sulfur on hysteresis at maximum cures.

a value of 0.20 corresponds roughly to a ΔT of 100° F in a Goodrich Flexometer. It has the advantage of being quick, and usually is more satisfactory for compounds likely to exhibit very high heat build-up, where the Goodrich Flexometer might be too drastic and cause blowouts.

The accelerator used with the various sulfur ratios for the compounds whose hysteresis values are charted in Figure 5 was tetramethylthiuram monosulfide. The quantity was within the optimum range for each sulfur level; the exact concentrations and hysteresis values are shown in Table VIII.

TABLE VIII

VARIATION IN HYSTERESIS WITH SULFUR CONTENT

Parts of sulfur	Parts of TMTMS	K at optimum cure (280° F)
0.5	2.0	0.290
1.0	0.50	0.257
2.0	0.40	0.222
3.0	0.25	0.204
4.0	0.20	0.196

It is evident that hysteresis, and presumably heat build-up, decreases perceptibly with increasing sulfur. The question arises as to the relative effect on hysteresis of the quantity and type of accelerator at different sulfur levels. As Table IX indicates, sulfur concentration is the controlling factor for hys-

TABLE IX

VARIATION IN TORSIONAL HYSTERESIS WITH ACCELERATION AT DIFFERENT SULFUR CONTENTS

Parts of sulfur	Parts of accelerator		K at optimum cure (280° F)	Relation of accelerator content to optimum concentration
0.5	TMTMS	2.0	0.290	Normal
	MBT	2.0	0.283	Low
1.0	MBT	1.0	0.269	Low
	MBT	2.0	0.248	Low
	TMTMS	1.5	0.240	Excessive
	MBT	1.0		
2.0	None		0.229	Low
	MBT	1.0	0.222	Low
	MBT	2.0	0.212	High
	Sulfamine	2.0	0.197	Excessive
3.0	MBT	2.0	0.203	High
	MBT	1.0	0.193	Normal

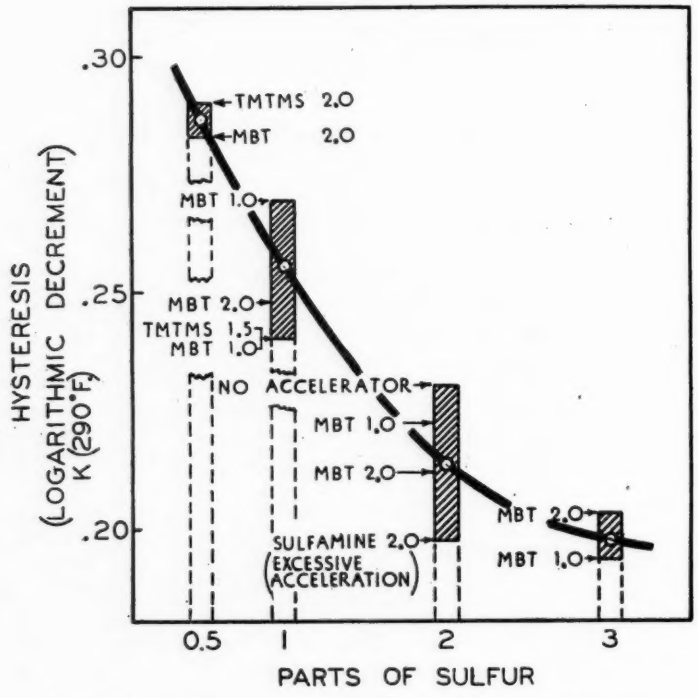

FIG. 6.—Relative influence of sulfur content and acceleration on hysteresis.

teresis, even in the presence of excessive concentrations of acceleration. It is interesting to note that a compound containing 2 parts of sulfur and no accelerator gave a hysteresis value at its optimum cure (10 hours) which fell within the upper range of the values reported for that particular sulfur level.

These data are shown graphically in Figure 6. It is evident that, within the range shown, sulfur content in general appears to establish definite maximum and minimum limits on the hysteresis values which may be obtained by variation of the type or quantity of acceleration. A curve drawn through the mean of the hysteresis values for each sulfur level does not vary significantly from the values shown in Table VIII and Figure 5.

At the highest sulfur level in Table IX, the larger quantity of accelerator gives a slightly higher value, which is opposite to the trend at lower sulfur levels. It has been noted frequently that hysteresis tends to rise sometimes on prolonged curing; this may explain this anomaly.

It is believed that the quantity of accelerator is likely to be more critical than the type in determining heat build-up characteristics, although when compared at their optimum ratios at 2 parts of sulfur, the thiazoles generally appear to give lower values than the dithiocarbamates (Figure 4). This might be expected from the lower modulus exhibited by the dithiocarbamate, as noted in Figure 3. Such differences as may exist, however, might be eradicated by an increase in sulfur content. The development of low heat build-up by adding excessive acceleration has the disadvantages of producing low tensile strengths and of causing undue embrittlement.

BRITTLENESS

Effect of Accelerators.—"Brittleness" is the term chosen to designate the tendency for nicks to grow and eventually to crack through, under dynamic flexing. Samples were rated from 0 to 10, after 50,000 flexures, according to the size of a crack present initially as a nick in the groove of a flexing sample. The angle of flexure in all cases was 45°, and the speed approximately 250 cycles per minute.

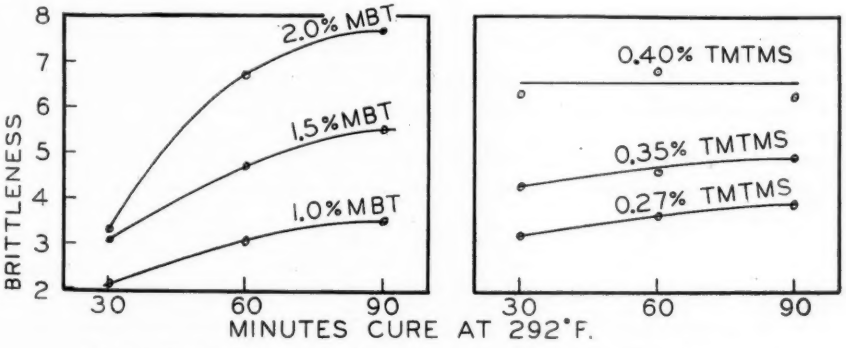

FIG. 7.—Effect of time of cure and increasing amounts of accelerator on brittleness.

Figure 7 shows the brittleness for three different concentrations of MBT and TMTMS over a range of cures. It is clear that increasing the concentration of accelerator results in progressively higher brittleness. Brittleness also increases with time of cure, although this is less evident for the thiuram which exhibits a flat curing curve.

Effect of Sulfur Content.—Sulfur levels were varied in compounds containing accelerators held at a constant level or within the range of optimum concentration; this was necessary in order to segregate as much as possible the effect of the accelerator. The variation in brittleness was as follows:

Parts of sulfur	Parts of TMTMS	Brittleness rating
0.57	0.35	2.6
2.00	0.35	3.7
4.00	0.20	5.2

The first two variations give a direct comparison of the effect of sulfur when the acceleration is kept constant. It was necessary to reduce the TMTMS content in the last case, otherwise the compound would have been overaccelerated. Results are recorded for the maximum cure in each instance.

Brittleness goes up as the sulfur content increases. The magnitude is not excessive, however, at the accelerator ratios employed, which suggests that the sulfur level is not the controlling factor in brittleness, as it was for hysteresis.

TABLE X

BRITTLENESS AND RELATIVE SULFUR AND ACCELERATOR CONTENT

Brittleness rating	*A* factor	Parts of accelerator		Parts of sulfur
2.6	Less than 1	TMTMS	0.35	0.50
3.1	Less than 1	MBT	1	2.00
3.7	Equal to 1	TMTMS	0.275	2.00
3.7	Equal to 1	TMTMS	2.00	0.50
4.6	Equal to 1	TMTMS	0.350	2.00
4.6	Equal to 1	MBT	1.50	2.00
5.2	Equal to 1	TMTMS	0.200	4.00
5.3	Equal to 1	Sulfamine	1.00	2.00
6.5	1 to 1.5	TMTMS	0.275	3.00
6.5	1 to 1.5	TMTMS	0.40	2.00
6.8	1 to 1.5	MBT	2.00	2.00
10	Over 1.5	Sulfamine	1.5	2.00
10	Over 1.5	TMTMS	1.00	1.00

Table X gives the brittleness ratings for a number of compounds containing various accelerators and sulfur concentrations. The relation between the actual accelerator content and the optimum concentration for that accelerator at the indicated sulfur content also is shown. For the sake of brevity this relation will be referred to as the *A* factor, and may be defined as follows:

$$A \text{ factor} = \frac{C}{C_{opt}}$$

where C = concentration of accelerator or accelerators in a compound
C_{opt} = concentration of accelerator or accelerator combination which develops maximum tensile strength in the compound

Thus *A* factors of less than unity, equal to unity, or greater than unity denote underacceleration, normal acceleration, and overacceleration, respectively.

It is evident that brittleness increases progressively with increasing ranges of the *A* factor. Any relation between sulfur content and brittleness appears to be masked by the concentration of accelerator expressed as the *A* factor.

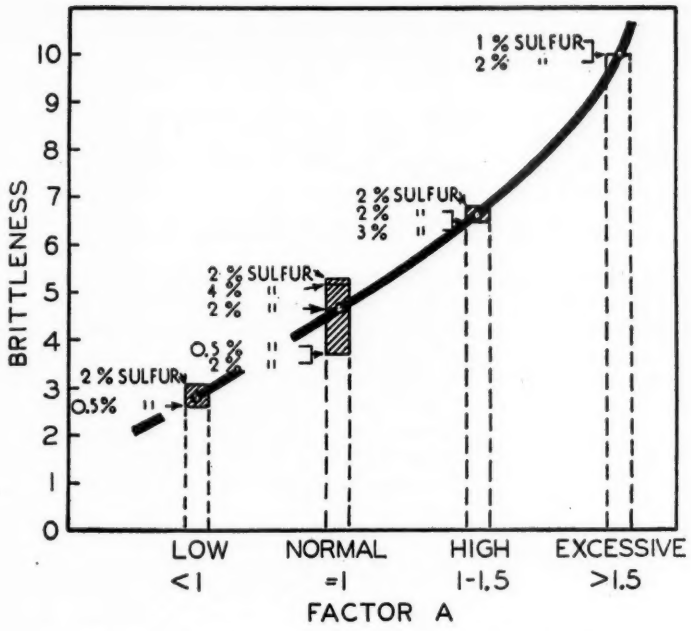

FIG. 8.—Relative influence of *A* factor and sulfur content on brittleness.

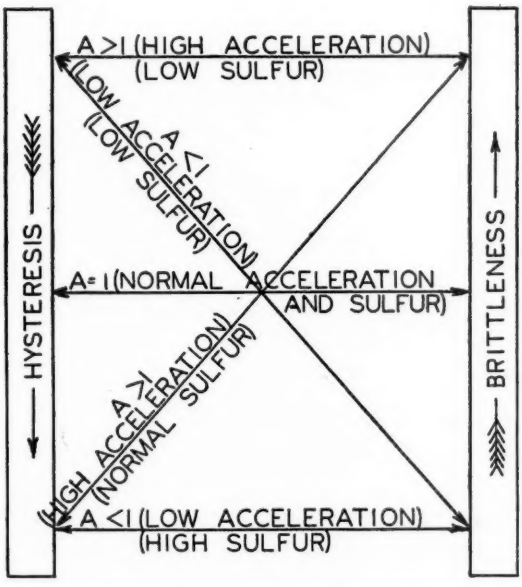

FIG. 9.—Schematic relation between hysteresis and brittleness for various values of *A* factor and sulfur content.

The data from Table X are charted on Figure 8 which may be looked upon as the counterpart of Figure 6. The *A* factor imposes definite maximum and minimum limits on brittleness which apparently cannot be exceeded by variation in the sulfur content. It seems reasonable to conclude, therefore, that the *A* factor, rather than sulfur content, is the controlling factor in embrittlement. It is interesting to recall that the antithesis of this relation was found to apply for hysteresis, where relative sulfur content, rather than acceleration, was the controlling element.

RELATION BETWEEN HYSTERESIS AND BRITTLENESS

It is clear from the foregoing sections that certain factors which tend to decrease hysteresis are also likely to increase brittleness. For example, increasing sulfur ratios, time of cure, and accelerator concentration all tend within limits to decrease hysteresis, but with a simultaneous increase in brittleness. This relation is shown in Figure 9, where relative values are plotted which

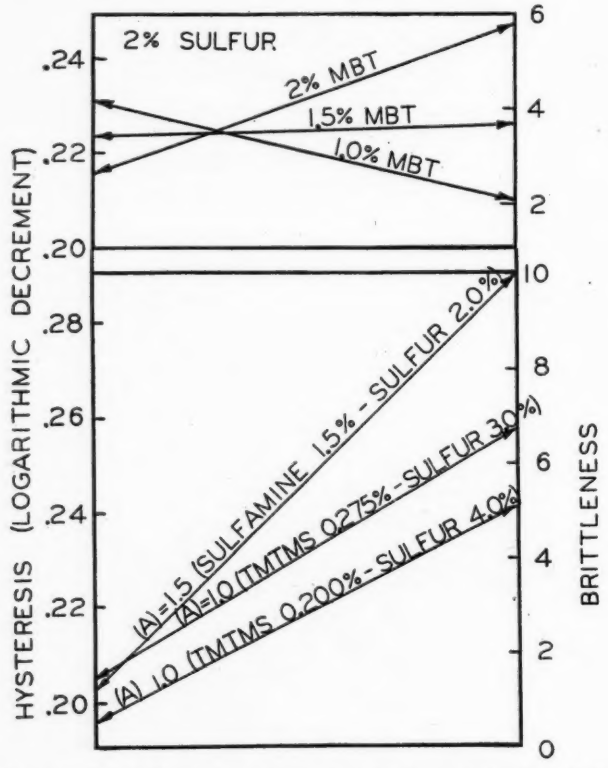

FIG. 10 (above).—Effect of increasing amounts of accelerator on hysteresis and brittleness.
FIG. 11 (below).—Relative influence of *A* factor and sulfur content on hysteresis and brittleness.

might result from: (*a*) an overaccelerated compound with a high sulfur content, (*b*) an underaccelerated compound with a low sulfur content, (*c*) a compound containing low sulfur and too much accelerator, (*d*) a compound which represents a compromise consisting of normal sulfur and accelerator ratios, and

(*e*) one containing high sulfur and low accelerator, which presumably would give the best results under service conditions requiring low hysteresis and low brittleness in the same compound. Actually the present data may be assembled on such a diagram.

Figure 10 charts the relative hysteresis and brittleness for three ratios of MBT in compounds containing 2 parts of sulfur. As the accelerator concentration increases, the hysteresis is seen to decrease, with a concomitant rise in brittleness. A service test would be required to pick the proper ratio to determine how much hysteresis could be sacrificed in order to achieve less brittleness, or *vice versa*.

The upper line of Figure 11 represents an attempt to reduce hysteresis by using a high concentration of an active accelerator. If the ensuing brittleness can be absorbed, this appears to be one solution to the problem; otherwise a compromise must be effected or another solution sought.

Data in Table X indicated that a high *A* factor (excessive acceleration) was the primary factor in inducing brittleness, whereas its effect on hysteresis was distinctly secondary to that exerted by the sulfur concentration. Conversely, higher sulfur contents, although capable of inducing low hysteresis, were not accompanied by excessive brittleness if the accelerator content was kept within its optimum range of concentration.

The two lower curves of Figure 11 show the results obtained with compounds containing 3 and 4 parts of sulfur, respectively, and acceleration within the range of optimum concentration for those sulfur levels. These compounds, containing the higher sulfur ratios with correspondingly lower acceleration, have produced low hysteresis without the development of excessive brittleness.

DISCUSSION

Several references in the literature[9] have indicated that Buna-S calls for somewhat lower sulfur and higher accelerator ratios than natural rubber. Two per cent of sulfur has been suggested as approximately normal.

During the course of this investigation an analysis of some of the fundamental relations involved points to the conclusion that a shift in the direction of higher sulfur and lower accelerator ratios may be a more promising approach to the problem of effecting the most efficient compromise between hysteresis and brittleness. This is supported by the following observations:

1. Other things being equal, higher sulfur concentration is the controlling factor in producing minimum hysteresis.
2. Other things being equal, minimum accelerator concentration is the controlling factor in producing low brittleness.
3. The combination of these two controlling factors, *i.e.*, high sulfur and low acceleration, in the same compound appears to produce the most efficient compromise between these properties.

The use of higher sulfur and lower accelerator ratios tends to lengthen out curing cycles, and the relatively slow vulcanization rate inherent in Buna-S is already considered to be a serious drawback. It is proposed that this might be minimized by using more active types of accelerator. It has been shown that certain members of the dithiocarbamate group are among the most active compounds available. Some members also exhibit extreme processing safety. There is also the possibility of coacceleration, in which the dithiocarbamate predominates, to reduce vulcanization times.

Admittedly several factors remain to be evaluated for compounds containing higher sulfur and lower ratios of a dithiocarbamate-type accelerator—for

example, resistance to abrasive wear, blooming tendencies, and an exact appraisal of the ultimate effect of the poorer aging which is certain to result from higher sulfur ratios.

The foregoing remarks apply essentially to compounds which must exhibit minimum hysteresis. Presumably all rubber products should be as free as possible from brittleness, but low hysteresis is not always essential. For this latter class of compounds, the dithiocarbamates offer the advantage of providing maximum vulcanization rates without resorting to excessive accelerator concentrations. Their lack of persistence resulting in a broader curing range may be a desirable feature.

For those compounds which require maximum aging characteristics above all else, low sulfur ratios obviously will be used. It has been shown that the dithiocarbamates are more active than the thiazoles for this type of compound, and it has also been established that they produce higher physical properties (Table IV).

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PROCESSING CHARACTERISTICS OF SYNTHETIC TIRE RUBBER *

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The processing characteristics of synthetic tire rubber, such as is being made in the government program, are sufficiently different from those of natural rubber to require different laboratory and factory treatment. Since the laboratory tests used for the evaluation of processing characteristics were developed for natural rubber, it is not surprising that they are not so satisfactory for synthetic rubber. The purpose of this paper is to discuss some of the characteristics of synthetic tire rubber, and to describe certain tests which have been found useful for evaluating different types of synthetic rubber or different compounds of the same synthetic rubber.

In the course of the development, it has been necessary to evaluate rubbers with a wide variety of processing properties. As production has increased, there has been less variation in the output from any one plant. As the newer and larger plants come into full production, we can expect greater uniformity from each plant and between different plants. We can also look forward to gradual improvements in processing characteristics. This development will be ensured by adequate laboratory methods for evaluating processing properties.

This discussion is based in part on variations encountered in development work and in part on the properties of the present production from one plant.

PROCESSING CHARACTERISTICS

Milling.—Synthetic rubber differs from natural rubber in several important respects. It is tougher and consequently tends to become hotter on the mill. Also it is shorter and less thermoplastic. These differences show up as a marked difference in milling behavior. When crude natural rubber is put on a cold mill, it is tough and knotty until well broken down. If the mill is heated to 180–200° F, the rubber quickly smooths out, becomes soft, and is easily pulled out to a considerable extent. Under similar conditions the synthetic material smooths out somewhat more quickly on the cold mill but remains rather tough and nervy. At 180–200° F, it becomes considerably softer, but also becomes short and weak and is rougher than on a cold mill. Some of the experimental rubbers become so short and weak that they crack on the edges or become lacy, and in extreme cases fall off the mill.

Heat softening.—With regard to oxidative or "heat" softening, tire-type synthetic rubber is intermediate between natural rubber and the oil-resistant butadiene copolymers. Under proper conditions it can be softened in hot air, but unless the conditions are carefully controlled, the operation may actually harden the synthetic rubber. This is due to the fact that the oxidation has a double effect, a breakdown and a sort of oxidation vulcanization. In the first stages of heating, breakdown seems to be predominant and the rubber softens. Subsequently, however, the vulcanizing action becomes predominant, and the rubber assumes a scorched appearance, becoming grainy, short, and hard.

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 34, No. 11, pages 1309–1312, November 6, 1942.

Breakdown.—Probably related to the heat softening action is the mill breakdown. The synthetic rubber does not break down so much as natural rubber does. Considerably more milling is necessary for adequate breakdown, and the breakdown is less obvious. Nevertheless it is important in subsequent operations. It is hard to describe accurately and should be observed on a laboratory mill. The breakdown can be obtained either before or after pigments are added. There is some indication that the addition of pigments facilitates breakdown. The important thing is that the overall milling must be adequate and that breakdown is favored by a cool mill and a tight one.

Tubing.—The fact that the hot stock is short and weak sometimes leads to trouble in tubing operations. When the extruded cross-section is thicker in the middle than on the edges, as in a complete tread and side wall, the stock flows faster in the thick section than at the thin edge. As a result, the edges must be pulled out. When the hot stock is too short and weak, this stretching results in cracked edges.

Calendering.—If the stock is properly compounded and mixed, it will friction and calender without particular difficulty in most cases. A calendered sheet may have more shrinkage than natural rubber and hence more tendency to check.

Tack.—Synthetic tire rubber is much less tacky than natural rubber. The stocks are moderately responsive to freshening with gasoline or benzene. A cement of the synthetic rubber stock is better. At present the best solution appears to be a cement of a natural rubber compounded similarly to the synthetic compound.

Laboratory mixing procedure.—The choice of a laboratory mixing procedure will depend on the object of the experiment. If one is trying to duplicate factory conditions, he should use a hot mill. On the other hand, if the object is to get the best batch for comparative evaluation, it is best to use a cold mill. In one procedure for general laboratory use, the rubber should be well broken down before pigments or softeners are added, although sulfur and activation zinc oxide may be added during the breakdown period. The softener should be added before the pigments, and the latter should not be added rapidly enough to cause the batch to break. This is especially true in the case of the hard blacks. The accelerator is added last. If the batch contains hard black, it should be thoroughly cooled and then remilled for a short time on a cold mill. On a 12-inch mill it is best to use not more than 300–400 grams of synthetic rubber in the batch. It is obvious that various modifications are possible, and that this discussion should be used primarily as a guide.

Factory mixing procedure.—Factory processing is essentially laboratory processing on a large scale, as modified by limitations of equipment and demands of production. The best breakdown and mixing are obtained on cool tight mills. This requires smaller batches and better cooling than is usually practical in the factory. Normally a factory batch will run hotter and in a thicker band on the mill than a laboratory batch. This results in less breakdown. Addition of black seems to facilitate breakdown under these conditions, and it may be advisable to keep the mill tight, add the black as soon as the rubber is running smoothly, and add other materials later. In a Banbury mixer, normal-size batches should be used to ensure adequate ram pressure. In general, more total milling is necessary with synthetic rubber than with natural rubber. At the same time "heat history" should be kept at a minimum.

A well mixed compound will process better in subsequent operations and have better vulcanized properties than one which is not well mixed. Trials

must be conducted on the equipment available in each mill room to determine the best balance between quality and output.

LABORATORY TESTS FOR PROCESSING

It is often desirable to evaluate processing characteristics in the laboratory, either for the selection of rubbers or for the selection of compounding materials. No single test has been found satisfactory.

For determining the processing characteristics of a series of experimental rubbers, the tests found most useful in this laboratory are Mooney viscosity, *Y* value, and milling behavior on the crude rubber, and Goodrich plasticity, milling behavior, and tubing index of a batch mixed from the rubber.

For comparison of compounding materials the mixing time, Goodrich plasticity, milling behavior, and tubing index are used.

Milling test.—Some indication of processing characteristics can be obtained from the 10-gram milling test. When an experimental rubber becomes too short and especially when it becomes lacy on a hot mill, it will probably give trouble in the factory. Differences among compounded batches can also be observed on the mill.

Mooney viscosity.—For measurements on crude rubbers, the Mooney plastometer appears to be the most satisfactory type. In general, a 4-minute viscosity at 185° F between 50 and 75 seems desirable, although some rubbers with higher viscosity have given good results and some with lower viscosity have given poor results.

If practical, it is probably more desirable to run viscosities at 212° or 225° F.

Y value.—If the shear force reading at 185° F (or higher temperatures) on the U. S. plastometer is plotted against time at half-minute intervals, a curve of the type shown in Figure 1 is obtained. The difference between the mini-

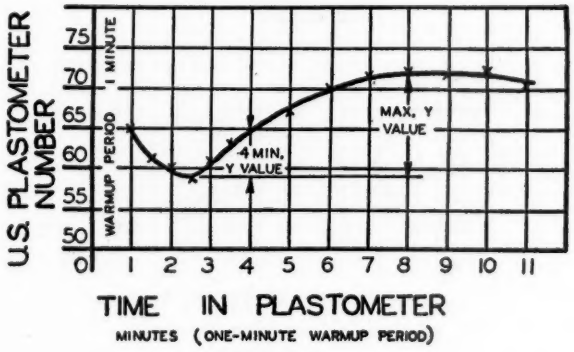

FIG. 1.—Shear force *vs.* time.

mum and the maximum readings is called the *Y* value. To expedite testing for factory control work, the first 4-minute portion of the shear force curve may be used. Under these conditions the 4-minute viscosity and the *Y* value for the initial 4-minute portion of the viscosity curve serve as indications of the processability of the rubber. A 10-minute determination is sometimes advantageous.

The *Y* value, as defined above, is a measurement of the shape of the time-viscosity curve. Since both mastication and heat softening alter the shape of

the time-viscosity curve, the Y value has limited applications. It may be used as a control test for evaluation of the rubber produced in synthetic plants.

Without going into any theoretical discussion, we may say that the rubbers with lower Y values are less nervy and mill better than those with high Y values. It appears that a Y value of 8 or less is desirable.

Goodrich plastometer.—For mixed stock, the Goodrich plastometer appears to give more useful information than the other types. Using a 5-pound weight at 185° F, a Goodrich plasticity of 25 or higher seems desirable for a tread type stock.

To determine the effect of "heat history", the laboratory-mixed stock without sulfur and accelerator can be heated in a press for several intervals and the plasticity determined. Indications are that, after 60 minutes at 300° F, the plasticity should still be at least half what it was before, and preferably should be over 20.

Tubing test.—A laboratory tubing test seems to be the most satisfactory single method of evaluation. For this purpose a batch containing 200 grams of rubber is mixed on the following recipe:

Synthetic rubber	100
Channel black	47
Zinc oxide	5
Paraflux	10
	162

This batch is mixed on a 12-inch mill, cooled for 24 hours, remilled, and again cooled. To simulate operating conditions, it is then warmed up on a mill at about 180° F, and tubed through a No. ½ Royle tube machine, likewise heated to about 180° F. Under these conditions the stock extrudes at about 230° F. The die has the shape and dimensions shown in Figure 2*A*. As the

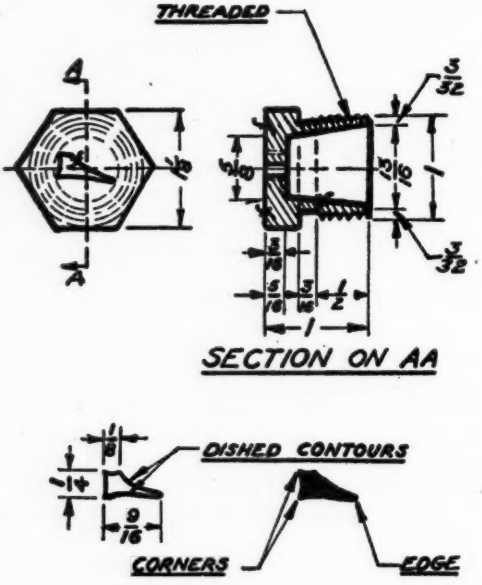

FIG. 2.—Details of die opening.

stock is extruded, it is pulled straight out from the die so that the narrow edge is pulled out. A small piece is cut from the best part of the strip and graded as follows:

1. The contour should be the shape of the die and not too swollen or porous. The best is 4, the worst 1.

2. The edge (Figure 2) should be smooth and continuous rather than rough, ragged, or broken. The best is 4, the worst 1.

3. The flat surfaces should be smooth and shiny, rather than wavy, dull, or lumpy. The rating is from 1 to 4.

4. The corners should be sharp and smooth rather than rounded or rough. The rating is from 1 to 4.

The tubing index is the sum of the four figures, and is followed in parentheses by the figures themselves in the order given. Thus the best tubing stocks would have an index of 16 (4444) and the worst an index of 4 (1111). The second figure, that for the edge, seems to be most critical and should be at least 3.

At present we feel that an index of at least 12 (–, 3, –, –) is necessary to give reasonably good processing in the factory. A set of standards, such as is shown in Figure 3, should be kept for comparisons.

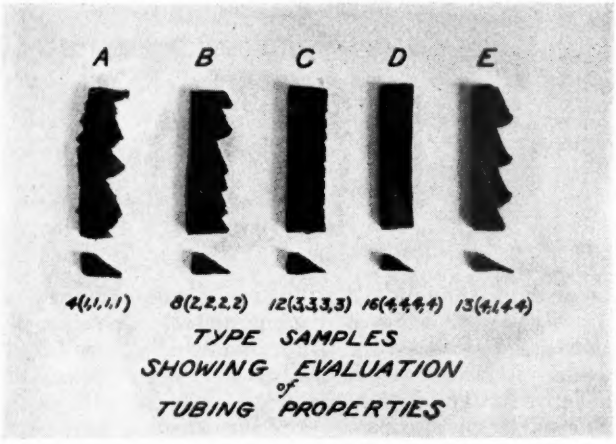

FIG. 3.—Type samples showing evaluation of tubing properties.

DISCUSSION OF PROCESSING TESTS

A high viscosity reading indicates a harder rubber, and a high Y value seems to indicate a more nervy one. Both of these characteristics make it harder to get proper mixing in the factory and cause the stock to run hotter, with resultant poorer mixing and tubing. A high Goodrich plasticity on the batch stock indicates good milling but not necessarily good tubing. Tubing characteristics are indicated by the tubing index.

Since laboratory mills can be run cooler and tighter than factory mills, it is often possible to obtain better mixing in the laboratory. This is especially true with harder and more nervy rubbers. When this occurs, the laboratory-mixed stocks will tube better than the factory-mixed stocks.

Based on the laboratory comparison of a considerable variety and number of experimental rubbers, the following conclusions have been drawn. When

the Mooney viscosity and *Y* value of the crude rubber are low and the Goodrich plasticity and tubing index of the mixed stock are high, the rubber will process well in the factory. If the reverse is true, it will not. When Mooney viscosity and *Y* value are high and Goodrich plasticity and tubing index are also high, there may be trouble in getting a good factory mix but, if such a mix is obtained, subsequent processing will be satisfactory.

TABLE I

DATA ON LABORATORY- AND FACTORY-MIXED STOCKS

Charge no.	Tubing index	Mooney 4-min. viscosity 185° C	Mooney 4-min. viscosity 225° C	*Y* value 185° C	*Y* value 225° C	Relative black dispersion (percentage)	Factory tubing temp. (° F)	Evaluation of tubing through plate die	Goodrich plastometer mixed batch[a]
1	Not run	98	..	18	..	75–80	250–255	Very poor	..
2	11 (2, 3, 3, 3)	98	74	11	8	80–85	240	Poor +	21
3	9 (1, 2, 3, 3)	85	..	14	..	...	240–245	Poor	..
4	8 (2, 2, 2, 2)	84	..	14	..	65–70	Not received	Poor	..
5	11 (2, 3, 3, 3)	83	71	16	9	75–80	245–250	Poor +	28
6	13 (2, 4, 3, 4)	77	..	11	..	80–85	230–235	Poor +	27
7	11 (2, 3, 3, 3)	76	..	11	..	85	225	Poor	9
8	8 (2, 2, 2, 2)	75	..	11	..	85–88	245–250	Poor	..
9	8 (2, 2, 2, 2)	73	..	14	..	65–70	...	Poor	..
10	13 (2, 4, 4, 3)	74	60	7	6	90	230–235	Poor +	24
11	12 (2, 3, 4, 3)	73	71	11	5	80–85	225–230	Fair	35
12	13 (2, 4, 4, 3)	72	64	10	6	85–88	225–230	Fair +	30
13	10 (3, 1, 3, 3)	70	..	11	..	75–80	230–235	Poor	..
14	9 (2, 2, 2, 3)	70	66	8.5	11	90	260	Poor	17
15	9 (3, 2, 2, 2)	69	..	10	..	85–88	Not received	Poor	24
16	11 (2, 3, 3, 3)	70	..	10	..	85–90	220	Fair +	38
17	13 (2, 4, 4, 3)	67	..	7	..	85–90	230	Fair −	..
18	13 (3, 3, 4, 3)	65	..	7.5	..	90–93	220	Fair +	33
19	14 (2, 4, 4, 4)	64	56	8	5	90–93	225–230	Fair	38
20	12 (3, 2, 4, 3)	63	54	7.5	7	90–93	225	Fair +	36
21	14 (2, 4, 4, 4)	..	..	..	..	90–93	220	Fair	..
22	13 (2, 3, 4, 4)	57	..	5	..	93–95	215–220	Fair −	48
23	13 (2, 4, 4, 3)	56	..	7	..	90–93	225	Fair	..
24	13 (2, 3, 4, 4)	43	..	8	..	93–95	210–215	Good	64
25	14 (2, 4, 4, 4)	40	..	3	..	95–98	210–215	Good	45
26	15 (3, 4, 4, 4)	40	..	2	..	95–98	210–215	Good	47

[a] 5 pounds at 85° C.

A series of charges made in regular factory operations were checked in the laboratory for viscosity, *Y* value, and tubing index. The same charges were then mixed into tread stocks in the factory and treads were tubed through a plate die. Data obtained in the laboratory and on the factory-mixed stocks are given in Table I. The *Y* value correlates well with the degree of black dispersion (determined microscopically) and the extrusion temperature. There is also good correlation between factory tubing results and predictions based on a combination of viscosity, *Y* value, and tubing index.

SUNLIGHT AND ACCELERATED LIGHT AGING OF SYNTHETIC RUBBERS *

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and

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Recently Werkenthin, Richardson, Thornley and Morris[1] reported on the sunlight and accelerated light aging of various natural and synthetic rubber stocks, and proposed a method for standardizing the accelerated light aging test. The purpose of the present paper is to provide data on the correlation of sunlight aging with accelerated light aging for various synthetic rubber stocks loaded with mineral pigments.

FORMULAS AND CURES

The formulas and cures for the synthetic rubber stocks are given in Table I. These stocks have a loading corresponding to a good quality, 40 per cent wire insulation compound. Most of the prominent types of synthetic rubber manufactured in this country and one foreign synthetic rubber were included in this study. It was necessary to blend Vistanex Medium with natural rubber, inasmuch as this synthetic rubber cannot be vulcanized.

Table I

	Vistanex M	Neoprene Type GN	Neoprene Type I	Thiokol Type F	Thiokol Type FA	Thiokol Type RD	Hycar O.R.	Chemigum Type I	Stanco Perbunan	German Perbunan
Vistanex-M	50.0	...	...	...	...	...	...	...	...	...
Smoked sheet	50.0	...	...	...	...	...	...	...	...	...
Neoprene Type GN	...	100.0	...	...	...	...	...	...	...	...
Neoprene Type I	...	...	100.0	...	...	...	...	...	...	...
Thiokol Type F	...	...	...	100.0	...	...	...	...	...	...
Thiokol Type FA	...	...	...	...	100.0	...	...	...	...	...
Thiokol Type RD	...	...	...	...	...	100.0	...	...	...	...
Hycar-OR	...	...	...	...	...	...	100.0	...	...	...
Chemigum Type I	...	...	...	...	...	...	...	100.0	...	...
Stanco Perbunan	...	...	...	...	...	...	...	...	100.0	...
German Perbunan	...	...	...	...	...	...	...	...	...	100.0
Lithopone	105.0	76.0	70.0	112.0	112.0	77.4	75.4	75.4	75.4	75.4
Zinc oxide	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Litharge	...	15.0	20.0	...	...	...	...	...	...	...
Stearic acid	.5	.5	1.0	.5	.5	1.0	1.0	1.0	1.0	1.0
Paraffin	2.0	2.0	2.0	...	...	2.0	2.0	2.0	2.0	2.0
Barrett No. 10 Oil	...	5.0	15.0	...	...	...	...	...	...	...
Neophax-A	...	10.0	...	...	...	...	...	...	...	...
Dibutyl phthalate	...	...	...	...	...	15.0	15.0	15.0	15.0	15.0
Tricresyl phosphate	...	...	...	...	...	15.0	15.0	15.0	15.0	15.0
Latac	...	.5	...	...	...	...	...	...	...	...
Neozone-A	...	2.0	2.0	...	...	...	...	...	...	...
Age-Rite Resin-D	1.5	...	...	...	...	...	1.5	1.5	1.5	1.5
Age-Rite White	.5	...	...	...	...	...	.5	.5	.5	.5
Altax	...	2.0	2.0	.45	.45	...	...	...	...	...
Diphenylguanidine	...	...	...	.1	.1	...	...	...	...	...
Santocure	.45	...	...	...	...	1.0	1.0	1.0	1.0	1.0
El-Sixty	.6	...	...	...	...	.1	.1	.1	.1	.1
Sulfur	1.15	...	1.0	...	...	1.5	1.5	1.5	1.5	1.5

* Reprinted from *The Rubber Age* of New York, Vol. 51, No. 3, pages 205–208, June 1942.

The stocks were mixed and cured in accordance with the methods recommended by the A.S.T.M. The cure giving the optimum tensile was selected for light aging.

PROCEDURE FOR LIGHT AGING

The procedure employed for determining the accelerated light aging of the stocks was essentially that described by Werkenthin and his coworkers[1]. The specimens, cut from ordinary test slabs, were $2 \times 6 \times 0.08$ inches. The specimens were held at 20 per cent elongation by stretching racks during exposure to the carbon arc in the National Eveready Model X-1A Irradiating Unit. The stretching racks were supported only on the upper part of the revolving frame in the irradiating unit.

Exposures were made to arcs from two types of carbons—the Eveready "Sunshine" carbon and the Eveready "U" carbon. No filters were used. Both exposures were continued until the more vulnerable stocks showed severe cracking, and it was judged that further exposure would deteriorate the specimens to such an extent that accurate determination of physical properties would not be possible. The exposure times were 56 hours to the "Sunshine" carbon arc and 24 hours to the "U" carbon arc.

These exposure times line up fairly well with the relative intensities of the ultraviolet light emitted by the arcs, as would be expected. Unpublished data obtained from the National Carbon Company show that the intensity of ultraviolet light in the range 2300–3300 Ångstrom Units is approximately 3.4 times greater for the "U" carbon arc than for the "Sunshine" carbon arc.

Specimens similar to those described above were exposed to direct sunlight for three months (September 23, 1941 to December 23, 1941) on the roof of the Rubber Laboratory at the Navy Yard, Mare Island. These specimens, maintained at 20 per cent elongation, were supported on a frame at an angle of 45 degrees with the horizontal, and faced south during exposure. Since exposure to sunlight did not cause severe cracking on any of the specimens, the period of exposure was set at three months for convenience.

RESULTS OF EXPOSURES

It is customary in papers on the light aging of rubber to include numerous photographs of exposed specimens. Usually these photographs have been reduced to a convenient size for printing so that none but the grossest details may be seen by the reader. Since there is no point in publishing photographs which are not clear to the reader, the authors have decided to deviate from the usual procedure by eliminating photographs in favor of a table (Table II) describing the surface appearance of the exposed specimens.

To make the descriptive data in the table understandable, it is necessary that the terms, *crazing* and *cracking*, be carefully defined. The authors define these terms as follows.

Crazing.—A network of very fine, irregular cracks in a resinous layer on the surface of the rubber. The cracks may run in any direction on the surface. The depth of the cracks is limited by the thickness of the resinous layer. The apparent thickness of the resinous layer is used as a measure of the degree of crazing.

Cracking.—A condition where cracks penetrate through the surface into the body of the rubber. The cracks may differ considerably in number, length and depth, depending on the severity of the light action and the innate char-

acteristics of the stock. All of the cracks run in a direction approximately normal to the direction of stretch.

Table II shows that all of the stocks were relatively unaffected by sunlight when judged by surface appearance. Although several of the stocks exhibited crazing, this form of deterioration is not considered to be as serious as cracking

TABLE II

EFFECT OF LIGHT AGING ON SURFACE APPEARANCE

Type of rubber	Exposed to "U" Carbon Arc		Exposed to "Sunshine" Carbon Arc		Exposed to Direct Sunlight	
	Exposed side	Back side	Exposed side	Back side	Exposed side	Back side
50% Vistanex-M 50% Smoked sheet	Slight cracking	No change	No change	No change	Crazing	Very slight crazing
Neoprene Type GN	No change	No change	No change	No change	Crazing	No change
Neoprene Type I	No change	No change	No change	No change	Very slight crazing	No change
Thiokol Type F	No change	No change	No change	No change	No change	No change
Thiokol Type FA	No change	No change	No change	No change	No change	No change
Thiokol Type RD	Cracking	No change	Very slight cracking	Slight cracking	Crazing	No change
Hycar-OR	Slight cracking	No change	Cracking	Severe cracking	Very slight cracking	No change
Chemigum Type I	Slight cracking	Cracking	Very slight cracking	Cracking	No change	No change
Stanco Perbunan	Slight cracking	Cracking	Very slight cracking	Cracking	Very slight cracking	No change
German Perbunan	———	———	Cracking	Severe cracking	No change	No change

from the standpoint of service requirements. Exposure to the carbon arc affected the surfaces more than sunlight in the cases of the Perbunan-type stocks[2] and the Thiokol Type RD stock, but about the same as sunlight in the cases of the Vistanex Medium stock, the Neoprene stocks, and the other Thiokol stocks.

Better correlation between sunlight aging and carbon arc aging was obtained when the extent of deterioration was based on change in tensile properties instead of on change in surface appearance. The initial and aged tensile strengths are charted in Figure 1, and the initial and aged ultimate elongations are charted in Figure 2.

It will be observed that the three aged values for the tensile properties of each stock are in fair agreement with one another. In other words, 24 hours' exposure to the "U" carbon arc or 56 hours' exposure to the "Sunshine" carbon arc produces deterioration in tensile properties closely equivalent to three months' exposure to winter sunlight. Both accelerated light aging procedures agree with the sunlight aging procedure in establishing the Vistanex stock, both Neoprene stocks, the Thiokol Type F and the Thiokol Type FA stock as having superior light resistance to the Thiokol Type RD stock and the Perbunan-type stocks.

It can be argued that the close agreement between the change in physical properties caused by the accelerated light aging procedures and the change in physical properties caused by the sunlight aging procedure was fortuitous, inasmuch as the sunlight aging of the specimens was arbitrarily discontinued at the end of three months. Be that as it may, at least a directional agreement would be expected if the radiations from the carbon arcs have an effect on the stocks comparable to sunlight. Except in the case of the Neoprene Type I stock, this directional agreement was found for all stocks.

The pronounced deterioration in tensile strength of the Perbunan-type stocks due to sunlight aging could not have been foretold by visual examina-

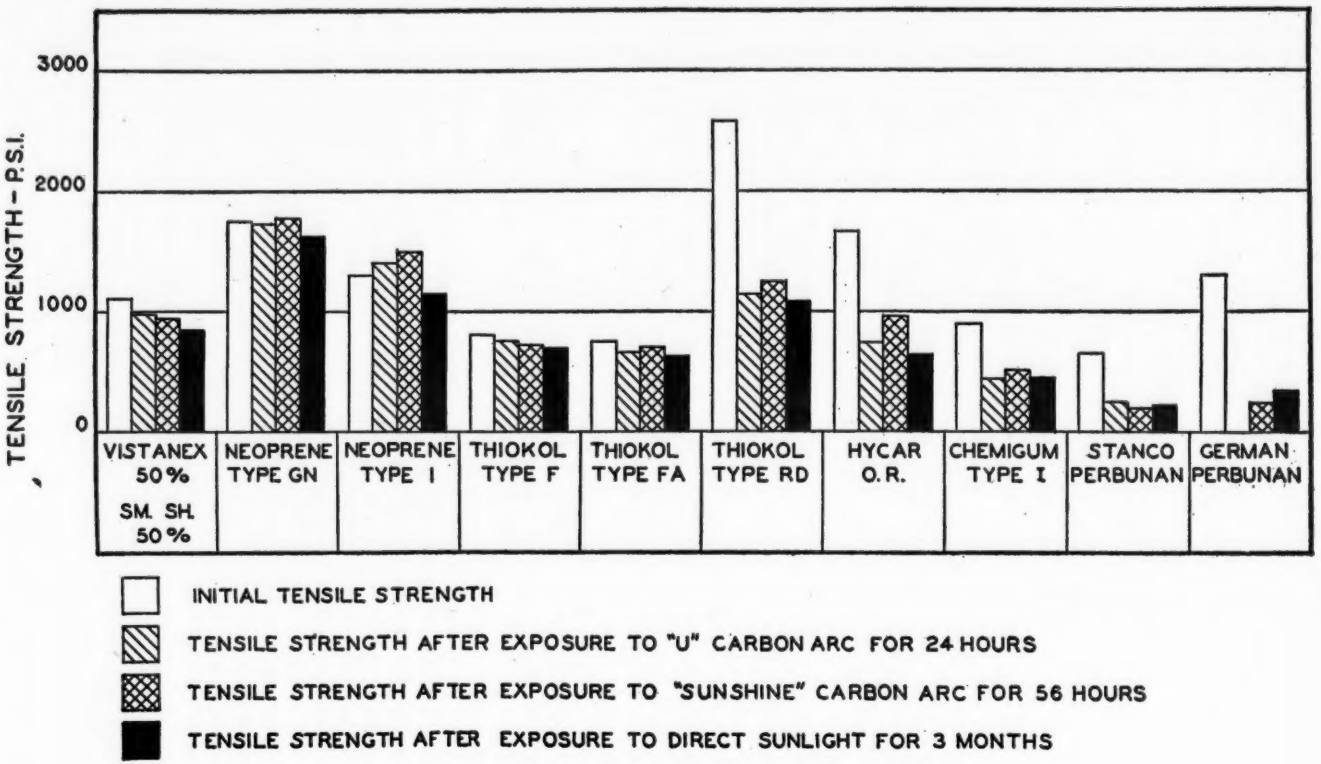

FIG. 1.—Effect of light aging on tensile strength of synthetic rubber stocks.

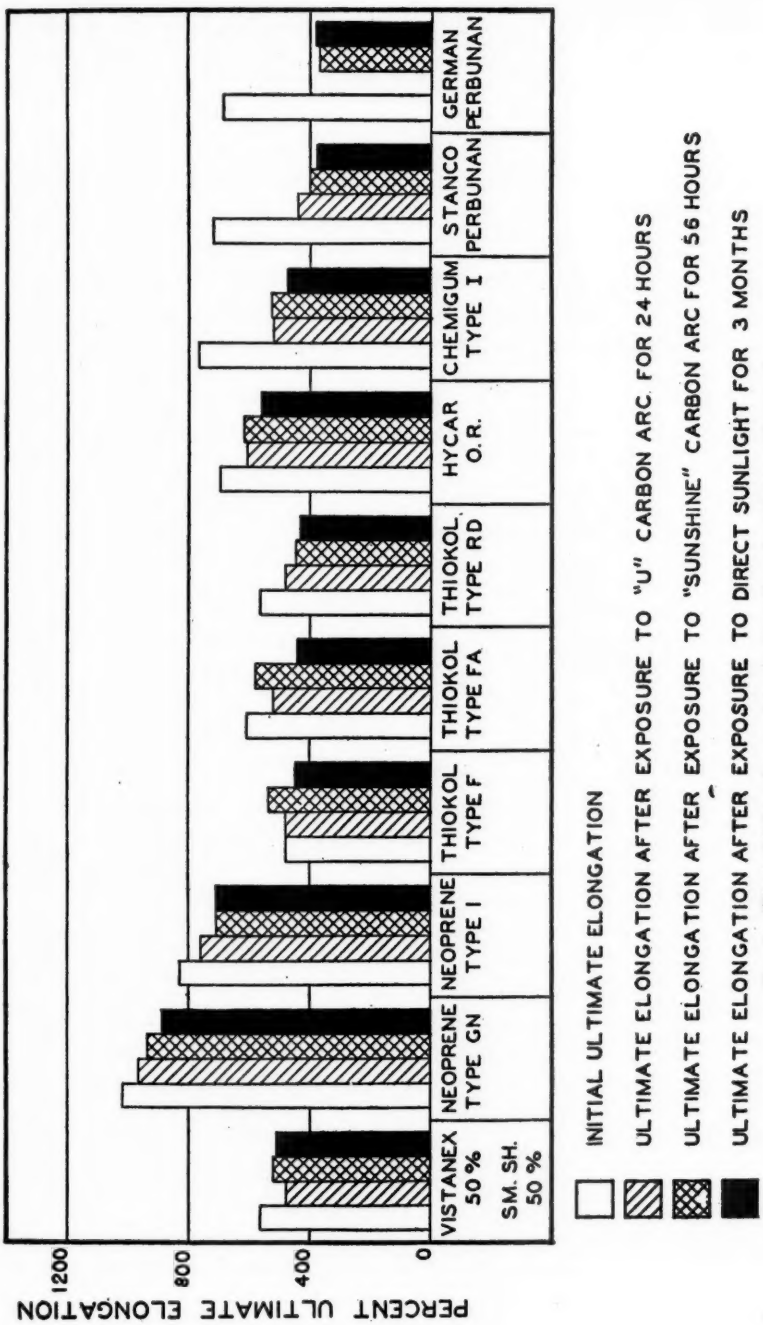

FIG. 2.—Effect of light aging on ultimate elongation of synthetic rubber stocks.

tions of the exposed specimens since none showed severe cracking. This conclusion provides further confirmation for the statement by Werkenthin, Richardson, Thornley and Morris[3] that visual examination alone cannot be relied upon to determine the extent of deterioration produced in vulcanized rubber by light.

ACKNOWLEDGMENT

The authors wish to acknowledge the coöperation of Irwin H. Whitthorne in this investigation.

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Hycar-OR, Chemigum (Type I), Stanco Perbunan, and German Perbunan are grouped as Perbunan type stocks.

Werkenthin, Richardson, Thornley and Morris, *India Rubber World* **105**, 143, 264 (1941).

NITROPARAFFINS AND DERIVATIVES AS HEAT-SENSITIZERS FOR RUBBER LATICES *

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Recent research has made various nitroparaffins and their derivatives available in commercial quantities[2], and large-scale applications for the materials are rapidly being found. A considerable number of these compounds cause heat sensitization in rubber latices[3], a phenomenon that has been produced in the past by a number of materials[4], and is used extensively at present in the manufacture of foamed-rubber products. The use of nitroparaffins in this application is quite new, however, and has recently been the subject of extensive experimentation in this laboratory.

In compounded latices it is not unusual to find three or more different materials, each with a definite purpose. In a study such as this, the use of completely compounded latices would unduly complicate the problem; so an effort was made to avoid these complications by running preliminary tests on the individual ingredients alone in a latex-nitroparaffin mix. It was found that gelling could not be produced by a nitroparaffin alone, even though the test mixtures were heated for considerable periods at 80–90° C. However, addition of a small proportion of zinc oxide to these mixes quickly induced gelling. It was also found that the oxides and hydroxides of the elements of Periods 2–6 of the Second Group of the Periodic Table gave results similar to those obtained with zinc oxide:

Formula:	Lotol NC-957	83 grams
	Nitroethane	1
	Metallic compound	1
Temperature		50° C
Compounds that produced gelling:		
Group II	MgO	4 min.
	CaO	6
	ZnO	8
	SrO	10
	CdO	17
	$Ba(OH)_2$[a]	0
	HgO	260
Compounds that produced no gelling:		
Group I	NaOH, KOH, Cu_2O, $AgC_2H_3O_2$	
II	BeO[b]	
III	B_2O_3, Al_2O_3, $La_2(SO_4)_3$	
IV	TiO_2, ZrO_2, $Sn(SO_4)_2$, CeO_2, PbO, $Th(NO_3)_4$	
V	H_3VO_4, As_2O_3, Bi_2O_3	
VI	CrO_3, MoO_3, Na_2WO_4, Na_2UO_4, UO_3	
VII	MnO_2	
VIII	CoO, FeO, NiO	

[a] Barium hydroxide always produced gelling when added to latex, even in the absence of nitroethane.
[b] A 0.1% suspension in water was used. When carefully added to a blank (no nitroethane), this suspension produced gelling in 108 minutes.

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 34, No. 9, pages 1106–1107, September 1942.

For use in subsequent tests, a sample of zinc oxide dispersion was prepared by ball-milling a composition prepared by the following recipe (in grams):

Zinc oxide (New Jersey Zinc Co., Horsehead Red XX4)	50
Dispersing Agent (Darvan, R. T. Vanderbilt Co.)	2
Water	50

In the course of experiments on the use of nitroparaffins and their derivatives as heat sensitizers, two different samples of latex were used: Concentrated F, from the Heveatex Corporation, and Lotol NC-957, from the Naugatuck Chemical Company. Both had been concentrated to 60 per cent rubber content by centrifuging, and the former had been protected against coagulation by the addition of ammonia.

TABLE I

NITROPARAFFINS AND DERIVATIVES AS HEAT-SENSITIZERS

(Formula: Concentrated F latex, 167 grams; ZnO dispersion, 4; heat-sensitizer, 2)

Compound	Gelling time (hrs.) 28° C	50° C	80° C
Nitroparaffins			
Blank	No gel	6.17	0.13
Nitromethane	48	0.22	0.05
Nitroethane	24	0.22	0.07
1-Nitropropane	48	0.45	0.07
2-Nitropropane	48	0.43	0.07
1-Nitro-2-methylpropane	96	0.55	0.10
2-Nitro-2-methylpropane	144	0.75	0.10
1-Nitrobutane	96	1.82	0.08
2-Nitrobutane	96	1.12	0.08
(1-Nitroethyl) benzene	No gel	2.77	0.08
Halonitroparaffins			
Chloronitromethane	288	1.17	0.07
1-Chloro-1-nitroethane	48	0.50	0.10
1,1-Dichloro-1-nitroethane	No gel	4.60	0.08
1-Chloro-1-nitropropane	48	0.50	0.10
1,1-Dichloro-1-nitropropane	No gel	4.60	0.10
2-Chloro-2-nitropropane	No gel	1.35	0.10
1-Chloro-3-nitropropane	24	0.20	0.05
1-Bromo-1-nitropropane	48	0.35	0.08
1-Chloro-2-nitrobutane	24	0.35	0.08
Nitroalcohols[a]			
2-Nitro-2-propanol	120	2.20	0.10
1-Nitro-2-methyl-1-propanol	240	3.33	0.10
1-Nitro-2-butanol	288	4.53	0.08
2-Nitro-1-butanol	192	4.53	0.12
2-Nitro-2-methyl-1-butanol	288	4.53	0.12
3-Nitro-3-methyl-2-butanol	120	2.13	0.08
1-Nitro-3-methyl-2-butanol	192	0.47	0.08
2-Nitro-1-pentanol	120	4.03	0.10
3-Nitro-2-pentanol	96	4.03	0.12
2-Nitro-3-pentanol	72	0.65	0.08
3-Nitro-3-methyl-2-pentanol	120	0.53	0.10
2-Nitro-2-methyl-3-pentanol	144	0.53	0.08
2-Nitro-3-hexanol	216	0.90	0.12
3-Nitro-2-hexanol	312	2.78	0.07
4-Nitro-3-hexanol	264	0.37	0.17
3-Nitro-4-heptanol	264	2.42	0.12
5-Nitro-4-octanol	264	3.25	0.12

[a] The nitroalcohols were added as 10% aqueous solutions, to prevent local coagulation; if added directly, coagulation occurred.

The compound to be tested was prepared in the following manner: The latex was stirred well, strained through cheesecloth, and weighed. The proper amount of zinc oxide dispersion was added to give 2 grams of the oxide per 100 grams of dry rubber. The compounds to be tested as heat-sensitizers were then added slowly to the latex with rapid stirring.

The determination of the gelling time was carried out in the following way. Forty cc. of the prepared latex were poured into a 25 × 200-mm. Pyrex test-tube. An iron wire 20 cm. long with a hook of about 1 cm. radius was placed in the latex. This assembly was stoppered with a cork having a groove down one side, through which the wire extended. The test-tube was placed in a thermostat at the desired temperature, and at intervals the liquid was tested for gelling by moving the wire gently up and down. Vigorous stirring was avoided, since this occasionally induced gelling. When the mass slipped readily in the tube, it was considered to be gelled, and the elapsed time was recorded.

In Table I the results of tests on a number of nitroparaffins and nitroparaffin derivatives are presented. All are shown to be heat-sensitizers.

TABLE II

EFFECT OF CONCENTRATION OF 2-NITRO-2-METHYL-1-PROPANOL ON GELLING RATE

(Formula: Lotol NC-957, 167 grams; ZnO dispersion, 4; 2-nitro-2-methyl-1-propanol as specified)

Nitroalcohol[a] (g./100 g. dry rubber)	Gelling time (hrs.) 28° C	50° C	80° C
0.25	...	96	4.67
0.50	288	23	3.00
1.00	192	11.22	0.28
2.00	30	1.13	0.12
3.00	22	0.33	0.09
4.00	4.72	0.20	0.08
5.00	4.33	0.14	0.07

[a] Added as a 25% aqueous solution.

TABLE III

EFFECT OF NITROETHANE ON VARIOUS DISPERSIONS

Revertex (75% solids) (g.)	133	...	...	...	...	...
Neoprene (50% solids) (g.)	...	200	...	...	...	...
Gray tube reclaim (50% solids)[a] (g.)	...	...	100	...	...	...
Red tube reclaim (50% solids)[a] (g.)	...	...	...	100	...	...
Whole tire reclaim (50% solids)[a] (g.)	...	...	...	...	100	...
Plantation crude (46% solids) (g.)	...	...	...	...	...	208
50% ZnO dispersion (g.)	4	4	...	...	...	10
Nitroethane	2	2	1	1	1	2
Gelling time at 50° C (hrs.)	Over-night	0.08	45	1	1	6

[a] The zinc compounds present in the reclaims were sufficient for the test so none were added.

In another series of tests, the highly water-soluble crystalline compound, 2-nitro-2-methyl-1-propanol, was used to study the effect of heat-sensitizer concentration on the rate of gelling under various conditions. The results are listed in Table II. Table II shows that compounds with a nitroalcohol concentration of three parts per hundred are stable enough at room temperature for most process requirements, and other tests have shown that they can be stored at 15° C for more than a month without gelling.

Nitroethane was tested in a series of artificial latices, and was found to be a vigorous heat-sensitizing agent for these compounds, none of which would gel without it. The results are listed in Table III.

The true rate of gelling at elevated temperatures is somewhat faster than the tables indicate, owing to poor heat transfer through the latex. Thin layers may be gelled quickly. When a test-tube full of water at 100° C was dipped into a sensitized latex and withdrawn after 5 minutes, its outer surface was coated with a layer of gelled rubber that was 23.8 per cent heavier than the layer deposited by a nonsensitized latex.

In another test, a 25 × 200-mm. Pyrex test-tube was filled with a sensitized latex to a depth of 50 mm., and was immersed in a thermostat at 90° C. At the end of 5 minutes the latex had gelled (according to the test described at the beginning of this paper), but the center of the mass had not yet reached 75° C. The true time of gelling at 90° C must, therefore, be appreciably less than 5 minutes.

REFERENCES

[1] Present address: Thermatomic Carbon Co., Terre Haute, Indiana.
[2] Hass, Hodge and Vanderbilt, *Ind. Eng. Chem.* **28**, 339 (1936); Gabriel, *Ind. Eng. Chem.* **32**, 887 (1940).
[3] Commercial Solvents Corp., U. S. patent application.
[4] Pestalozza, U. S. patent 1,717,248 (1929); 1,750,540 (1930); Dunlop Rubber Co., British patent 351,937 (1930).

TECHNICAL MICROSCOPY IN THE RUBBER INDUSTRY *

R. P. ALLEN[1]

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For supplying information not obtainable by the usual methods, the microscope is useful and often essential; not only will it disclose details which would otherwise be unseen, but by its unique methods of examination measurements of certain properties of materials can be readily secured which are not otherwise obtainable.

When one considers the value of the microscope to the rubber industry specifically, the study of the size of particles is usually the first and frequently the only application which comes to mind, although other uses have been suggested and described[2]. The present paper not only describes the importance of the microscope in determining particle size and shape, but also covers its applications in the solution of other problems which ordinarily are not considered to lie in the field of microscopy. [Chamot[3] describes many interesting applications in different industries which indicate the unusual capabilities of microscopic methods.]

In a well-organized industrial laboratory, the microscope is used to supplement and aid other methods for examination of raw materials, control of factory processing, correlation of physical properties with service performance, and solution of factory difficulties. The specific examples cited in this paper represent uses which have originated in connection with the manufacture of rubber goods, but they serve also to illustrate methods applicable to problems of the same type originating in other industries.

EXAMINATION OF RAW MATERIALS

For the accurate evaluation of pigments used in rubber, the size and shape must be known accurately. Foreign material must be identified when it is present. Most of the microscopic methods used for measurement of particle size are described in an excellent summary by Chamot and Mason[4]. Those methods invariable depend primarily on direct observation of the individual particles, but indirect methods are also useful. For example, Pohle[5] employed a "mass color effect" for determining the presence or absence of small particles; thin sections of rubber compounds loaded with pigments containing a high proportion of "colloidal" particles, such as channel blacks, exhibit a reddish-yellow transparency which may be distinguished easily from the neutral gray observed where the particles are largely noncolloidal. In the Goodrich laboratory also, this Tyndall phenomenon has been found useful. This effect was utilized quantitatively by Stutz and Pfund[6] and later by Stutz[7] alone is measuring the average particle size of zinc oxides.

The methods of determining particle size may logically be divided into two classes, those applicable to particles above the limit of resolution of the micro-

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scope and those applicable below that limit, although few commercial pigments contain particles which in size lie entirely in one class or the other.

General aspects of the measurement of particle size.—In 1923 Perrott and Kinney[8] discussed the factors of fundamental importance in the use of particle size measurements. From one set of measurements obtained by microscopic observation, these authors showed that an "average particle size" may be calculated with respect to number, length, surface, or volume, and that the significance of an average particle size depends on which average is chosen for use. For example, Figure 1 shows a representation of the powdered coal with

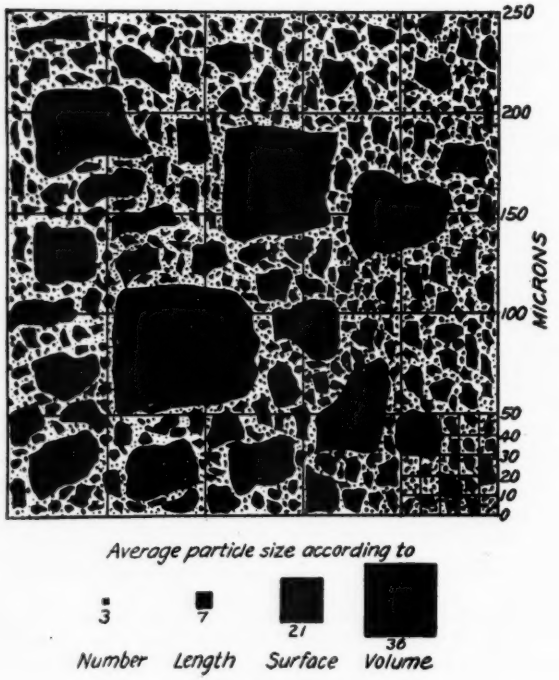

FIG. 1.—Powdered coal.
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which Perrott and Kinney worked and the several averages obtained, these ranging from the average of 3 microns based on number to the 36 microns based on volume. Figure 2 shows diagrammatically the approximate distribution of particles in the sample of powdered coal by number, by diameter, by surface, and by weight. By number the small particles clearly predominate, but by weight it is observed that relatively few of the larger particles are sufficient to balance a very large number of the smaller particles. Although this powdered coal is a material much larger than rubber or paint pigments, the difference in the "average sizes" is relatively as great for smaller particle sized pigments, since the nonuniformity is fundamentally responsible for the differences in the averages based on number, diameter, surface, or volume.

The differences between these averages obviously indicate the necessity for obtaining that average particle size which is most significant in a specified use.

Haslam[9] attempted to determine the rational choice for rubber technology. Using zinc oxides of different particle sizes, he found the $\bar{d}_1$ "diameter" to give essentially no correlation, $\bar{D}$ to give some correlation, and $\bar{d}_3$ to give fair correlation with the physical properties which the oxides imparted to the rubber compositions. [$\bar{D}$ expresses "the diameter of a hypothetical sphere such that

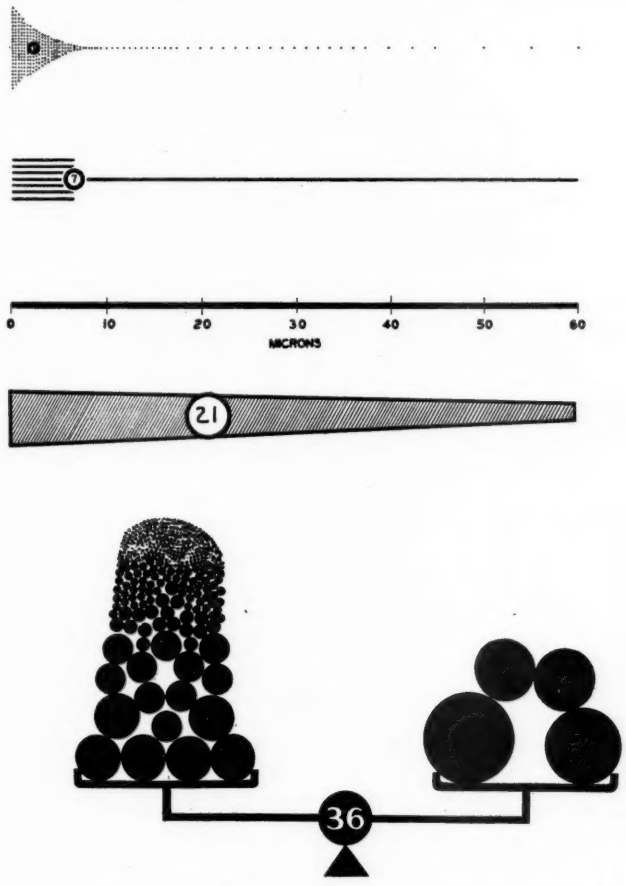

FIG. 2.—Distribution of particles in powdered coal.

the volume of n such spheres is equal to the actual volume of n particles"[10]]. No calculations of the $\bar{d}_4$ diameter or results based on that value were presented, but the author's experience has indicated the $\bar{d}_4$ diameter to be of primary importance in rubber technology. By its use, one can determine best the ratio of the active to the inert fractions of a given pigment. This is illustrated by the following example:

Figure 3 is a photomicrograph of a carbon black of rather large particle size, while Figure 4 shows size-distribution curves of this pigment. One curve is the size-distribution based on diameter, the other is based on weight. The difference between the two curves is obviously large, this difference being

evaluated quickly from the cumulative per cent curves (Figure 5). On the $\bar{d}_2$ curve the "average particle diameter" is 0.4 micron, a value on either side of which lies half of the sum total of the diameters of the particles; but the

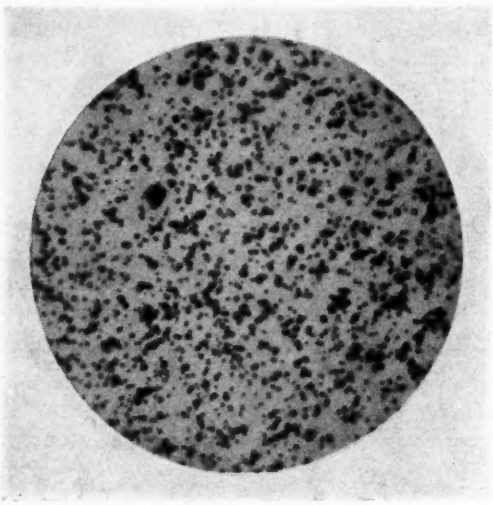

FIG. 3.—Carbon black.

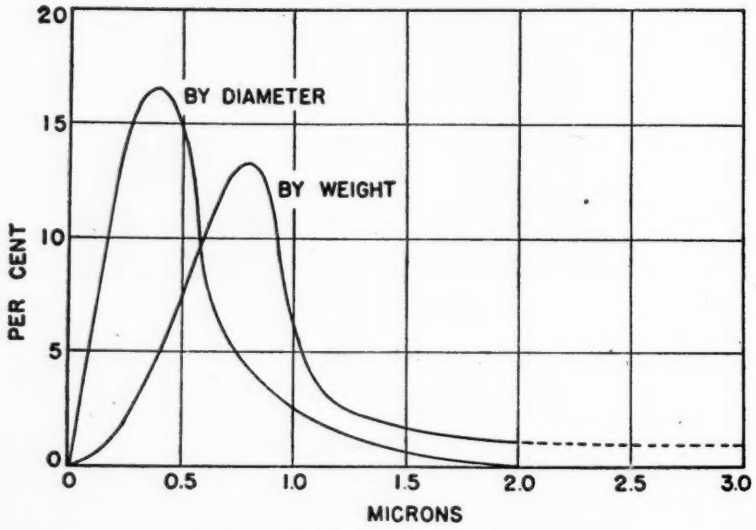

FIG. 4.—Size-distribution curves of carbon black.

"weight" curve indicates that only about 10 per cent by weight of the particles lie below 0.4 micron while 90 per cent by weight comprise the fraction above this point. Which curve is most significant in evaluating the behavior of this pigment?

On the basis of physical tests of rubber compositions, 0.6 micron may be reasonably picked as the approximate dividing line between a nonreinforcing and a reinforcing pigment. At that point, the curve based on diameter indicates that nearly 75 per cent of the particles of this material possess reinforcing

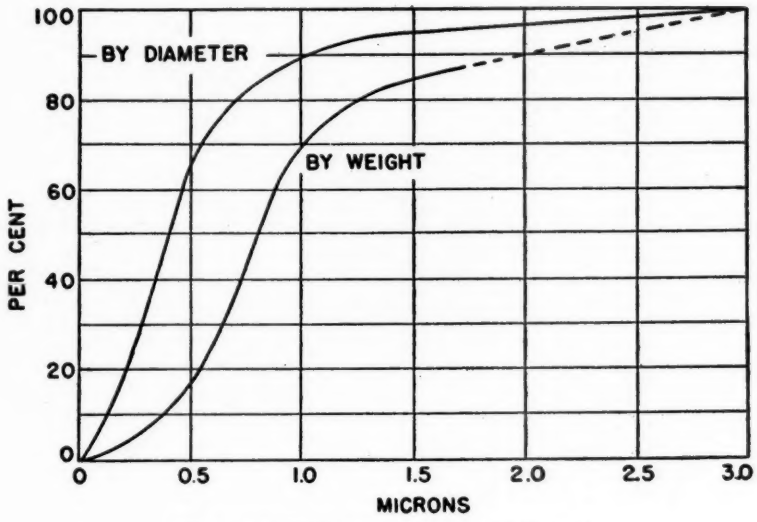

FIG. 5.—Cumulative per cent curves of carbon black.

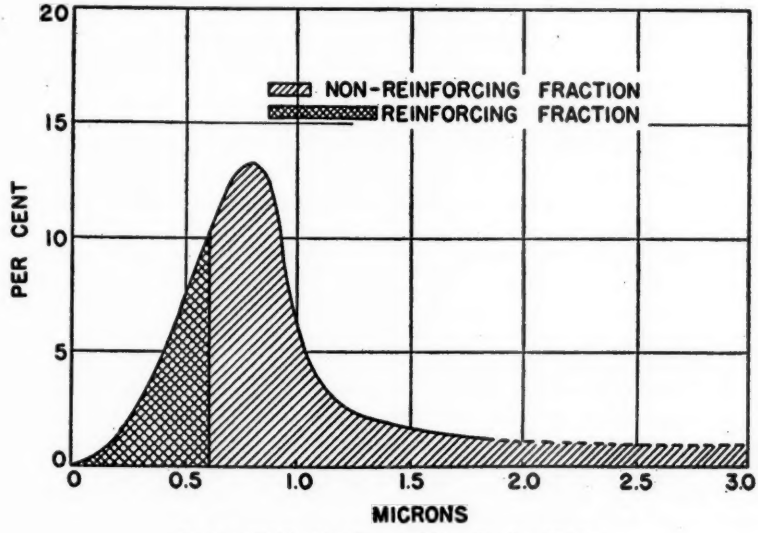

FIG. 6.—Reinforcing characteristics of carbon black.

characteristics, a conclusion which is inconsistent with the properties imparted to rubber by this material. In contrast, the curve based on weight indicates that only about 25 per cent of the particles comprise a reinforcing fraction, as shown in Figure 6, and this is more consistent with the performance of the

pigment in rubber. This may be visualized in another way: 20 volumes of this carbon black added to 100 volumes of rubber incorporate 5 volumes of reinforcing particles and 15 volumes of particles with no reinforcing value.

To procure the data necessary to calculate any of these "average sizes" is a laborious task. For example, Green[11] mentions seven hours as the required time for five samples of zinc oxide. Obviously, these time-consuming methods should be avoided, yet values must be supplied which will accurately indicate the behavior to be expected of the sample in rubber. Since the microscopist in a rubber laboratory is called upon to report on the particle size of many pigments each day, the question of technique and method to be used thus becomes of paramount importance.

The first step in the measurement of particle size is the preparation of a suitable mount. The method employed in the Goodrich laboratory has been described recently by the author[12]. For microscopic examination of the mount, nothing short of perfect optical conditions can be tolerated if an accurate final result is to be obtained. For pigments of 5 microns and under, dark-field is used, not only that every particle may be more readily observed, but also because of the possibility of obtaining some idea of the size of particles below the limit of resolution.

For illumination, a 108-watt, 6-volt ribbon-filament lamp fitted with an aspheric condenser is employed, placed to give a parallel, correctly centered beam. A cardioid dark-field condenser is fitted to the substage of the microscope. The most commonly used optics is a 4-mm. dry apochromat (N. A. 0.95) with correction collar, and an $\times 20$ compensating eyepiece fitted with an ocular micrometer with graduations equivalent to 1.25 microns. For a few pigments a dark-field condenser, *e.g.*, the Zeiss of "Leuchtbild", which permits the use of an objective of N. A. 1.30 is useful. Critical illumination must be employed, and the cover glass correction must be adjusted to the minimum of spherical aberration. The optical requirements throughout are simple but rigid.

On the sample under examination, the observer proceeds to construct mentally a size-distribution curve. If necessary, he prepares a mount of a standard sample from which a size-distribution curve has been prepared accurately, and uses this as a means of refreshing his memory. Using the specific optics just mentioned, particles down to about 0.4 micron (theoretically 0.33 micron) may be resolved. The observer notes the minimum and maximum size, and makes an estimate of the per cent by weight above and below 0.4 micron. The size of the particles below 0.4 micron, which are not resolved under the described conditions, may be judged on the basis of the decrease in intensity of diffracted light with decreasing particle size. The fraction above 0.4 is, in most pigments, of greater consequence in fixing the average particle size than the fraction below 0.4 micron, but neither fraction may be neglected. Having performed mentally these separate steps, the observer makes an estimate of the average particle size based on weight. Figures 7 and 8 summarize some of the steps in this procedure. Figure 7 is a photomicrograph of a standard iron oxide (left), and of an iron oxide (right) which was sent in for evaluation, and Figure 8 is a copy of the report which was sent to the Raw Materials Division on this particular sample. It is extremely rare that such a particle size evaluation fails to indicate precisely the properties which an unknown pigment will produce in rubber.

The success of this method depends primarily on the proper use of a dark field, which permits a rapid determination of the distribution of particle sizes.

In the author's opinion, dark-field methods should be more commonly employed. This lack of use may have resulted, partially at least, from various discouraging notes in the literature—for example[13], "While centering the con-

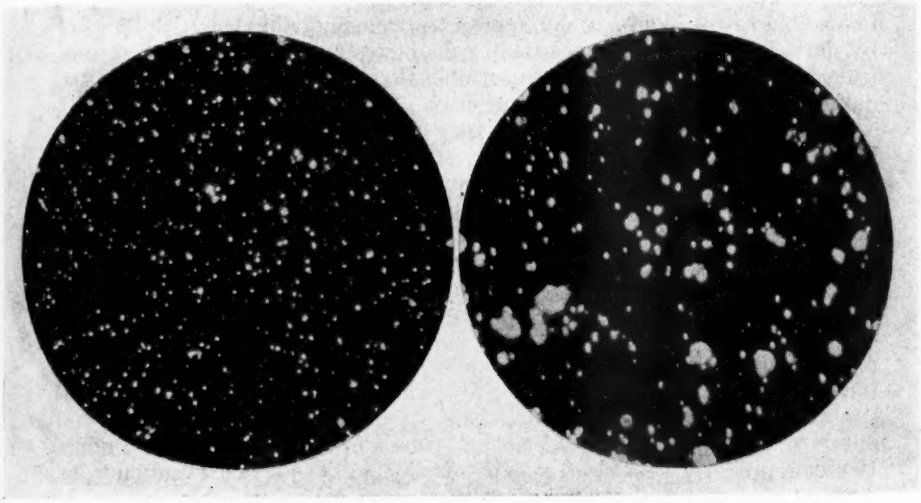

FIG. 7.—Iron oxides (× 1000).

November 21, 1938.

Mr. John Doe,
Raw Materials Dept.

Code XYZ

This sample of iron oxide is considerably coarser than our type. It shows a larger maximum size, a higher average size and a different size-distribution. Undoubtedly it possesses less tinting strength than our standard iron oxide.

The particles in Code XYZ have the same shape as those in the type; i.e., essentially spherical.

	Min.	Max.	Aver.	% by Weight Below 1 mu
Standard iron oxide	0.1	2.0	0.7	80
Code XYZ	0.1	5.0	1.7	20

Microscopic Laboratory.

Per M

FIG. 8.—Report on iron oxide.

denser and objective is important with a bright-field condenser, it is far more important . . . with a dark-field condenser", a statement which implies that slipshod manipulation will result in some sort of an image with bright-field,

while with dark-field perfect technique is imperative; it is obvious that perfect technique should be employed with all methods. Even technicians otherwise faultless have contributed to the impression that dark-field is of little value[14]. "Nothing is gained, and in fact a great deal lost, by attempting to employ dark ground illumination, or the ultramicroscope. In this latter case it is impossible to distinguish small aggregates from individual particles". Since by dark-field it is readily possible to distinguish agglomerates or aggregates from individual particles it is regrettable that this most useful capability of dark-field should be reported erroneously.

This general procedure is satisfactory for the majority of rubber pigments, but for one important class—namely, those rubber reinforcing pigments in which all the particles lie below the limit of resolution of oil-immersion objectives (about 0.20 micron)—a different procedure is needed.

Method for particle size measurement below the resolving power.—Bright-field microscopy using ultraviolet light offers some advantage in increased resolution[15] of small particles, but has not proved of extreme value in the study of channel gas blacks. It has been appreciated that size-distribution curves of these materials would be of great value, as they are with larger particle sized pigments, but it is only recently that these curves have been obtained. Parkinson[16], in an admirable investigation by centrifugal fractionation, reports the size-distribution curve for channel black. Equally fascinating are the results obtained with the electron microscope, the work of Wiegand and Prebus[17]. It seems probable that electron microscopy may be utilized eventually even for control purposes, but at present the results are most interesting in their theoretical application in the study of channel black.

In the Goodrich laboratory, one aim has been the development of a method for particle size evaluation in this region below the resolving power which would be accurate and suitable for control purposes. For these pigments, the first method[18] used was an adaptation of the Siedentopf-Szigmondy[19] procedure with gold sols. A small, known amount of carbon black was dispersed in the cleanest available rubber, and the number of particles of black in a small volume were counted in a dark-field microscope. From the concentration of black, the density of the black, and the number of particles counted in the known volume, the average diameter could be calculated. This average is the $\overline{D}$ diameter.

The method was not very satisfactory because of the inevitable presence of small particles in the rubber itself, which made necessary a large and somewhat uncertain correction factor. Gehman and Morris[20] made a notable advance in this art by dispersing carbon black in rubber, then making a cement with a clear, colorless mineral oil, such as Nujol. Thus, by the use of an optically empty diluting medium, the concentration of carbon black particles is reduced to the point where they may be separately observable in a dark-field microscope, and the correction for the foreign particles in the mixed dispersion medium is minimized. This count method has been investigated by a committee for the A. S. T. M., with the aim of discovering the sources of error which at first prevented concordant results among different laboratories[21].

This "proposed" method is now used extensively for particle size measurements in the region below about 0.20 micron. It is used frequently also for pigments in which the particles are predominantly above this limit of resolution and for which other methods should be used because of the distinct nonuniformity of sizes. In such instances, this D diameter is smaller than an average size based on weight (D_4). The erroneous results in rubber technology have

been pointed out earlier in this paper. Nevertheless, this method is invaluable for the measurement of particle sizes below the limit of resolution and for determining differences, for example, in various lots of the same type of pigment. Its principal disadvantage lies in the amount of time required and in the tediousness of the counting. To avoid these practical difficulties, a relatively fast and accurate method has been developed in the Goodrich laboratory.

This method for channel blacks was developed in 1930, and may be characterized as a combination of the Siedentopf-Szigmondy principle and the method of the author published in that year[22]. It depends on the observation of two microsections of rubber, containing the same concentration of the pigment under examination, placed in juxtaposition on the slide. In carrying out this method, 90 parts by weight of the cleanest available rubber and 10

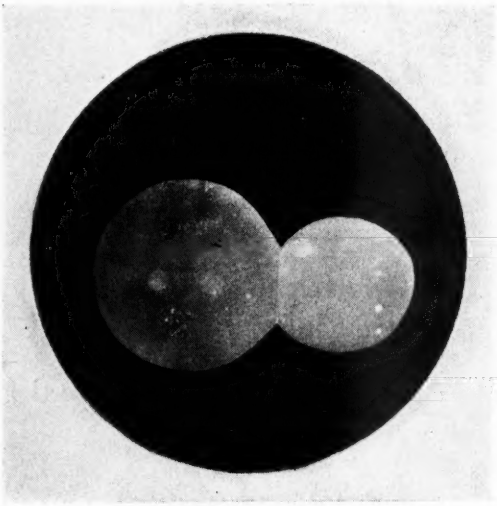

FIG. 9.—Channel blacks (×15).

parts of the specimen carbon black are mixed on a small rubber mill, with scrupulous care to avoid loss and contamination. Perfect dispersion must be secured, this being judged by a prescribed method[22]. Next, a small amount of the master batch is diluted by mixing with clean rubber, on a 12-inch roll mill, to a finished concentration of 0.1 per cent of black. The presence of the inevitable foreign particles in rubber is of minor consequence with concentrations of carbon black as high as 0.1 per cent. The stock thus prepared is mounted under the same cover glass, side by side with a similar stock containing a standard carbon black, the particle size of which has been measured, for example, by the count method. In the completed preparation, which should be about 1 micron thick, the two small pieces should just touch but not merge. This is shown in Figure 9 at low magnification.

In a sense this procedure is an application of the principle of the comparison microscope, for by it two separate objects, of the same pigment concentration and thickness of section and illuminated with the same condenser, may be observed with the same objective. The preparation of Figure 9 is shown at

higher magnifications in Figure 10. These two specimens represent two channel blacks, one of which has an average of 0.065 and the other of 0.092 micron as measured by the count method. Observation in the microscope shows interesting differences. First, at low magnifications (×100 to ×400) the

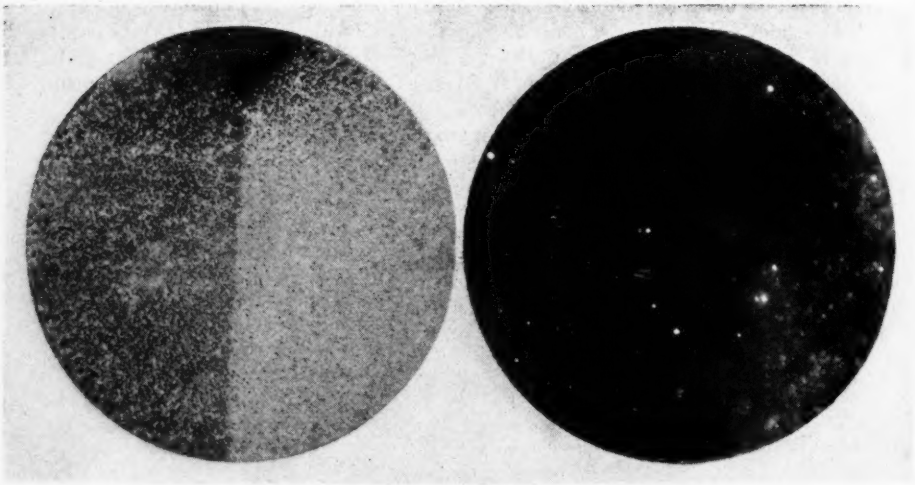

FIG. 10.—Channel blacks.
Left, ×100.
Right, ×100.

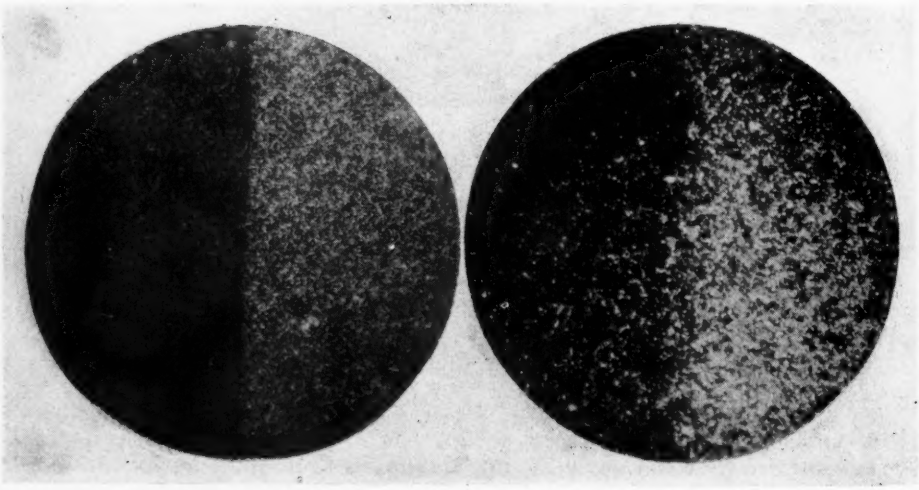

FIG. 11.—Thermal decomposition blacks (left) and zinc oxides (right) (×300).

larger sized black gives in general a more brilliant image than the smaller. Closer examination reveals that this occurs largely because of the higher content in the 0.092 sample of the large sized particles in these pigments. Second, at higher magnifications (×800 to ×1500) it may be observed that the total

number of particles is greater in the 0.065 sample, which may be expected because the average size is smaller. This high magnification observation is revealed only imperfectly in Figure 10 (right).

An unknown carbon black is thus compared with one or two standards, close observation being given to the relative number of the larger particles and the total number of particles in equal volumes. It is possible by this method to estimate rather accurately the average particle size of the unknown, the method having a precision of the order of 0.01 micron in the range from 0.05 to 0.10. The figure obtained is equivalent to the *D* diameter and because of the uniformity in particle size of channel blacks, it is sufficiently good to provide an evaluation of the material in rubber, even for such a significant property as tread wear.

As a matter of general interest, two other pairs of small particle sized pigments are shown in comparison by this method (Figure 11), two thermal decomposition blacks and two zinc oxides. The method extends considerably the use of the microscope as an effective and rapidly operable tool for the comparative study of pigments which are below its resolving power.

One of the blacks is P-33 carbon black, the other an experimental P-33 (smaller). For these samples and permission to publish, grateful acknowledgment is made to R. B. Moore, formerly with the Thermatomic Carbon Company, and to A. W. Campbell of the Commercial Solvents Corporation.

The zinc oxides are Kadox and an experimental Kadox (smaller). For these samples and permission to publish, grateful acknowledgment is made to the New Jersey Zinc Company.

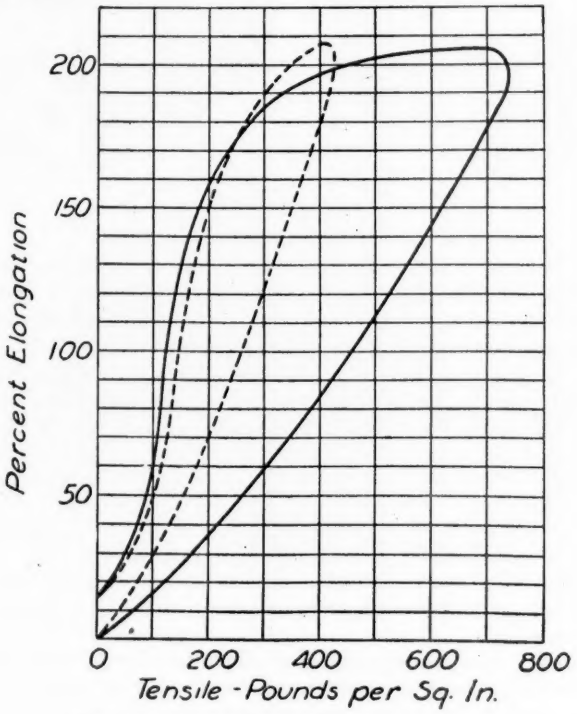

FIG. 12.—Hysteresis loops of two rubber compounds.

Observation of particle shape.—For many years it was suspected[23], and gradually became known, that any pronounced departure from a spherical shape of the individual pigment particles produces a rubber compound with characteristic properties. Most clays, some magnesium carbonates, some zinc oxides, some whitings, and a few other pigments in rubber impart properties which may be related directly to the needlelike or the platelike shape of the particles. Among the properties which are profoundly affected by a nonspherical shape is the hysteresis of a rubber compound. Figure 12 shows the first hysteresis loops of two rubber compounds, one of which contains 20 volumes of a spherical zinc oxide; the other, showing the greater hysteresis loss, contains an equal quantity of a zinc oxide of predominantly acicular shape. The respective oxides are shown in Figure 13.

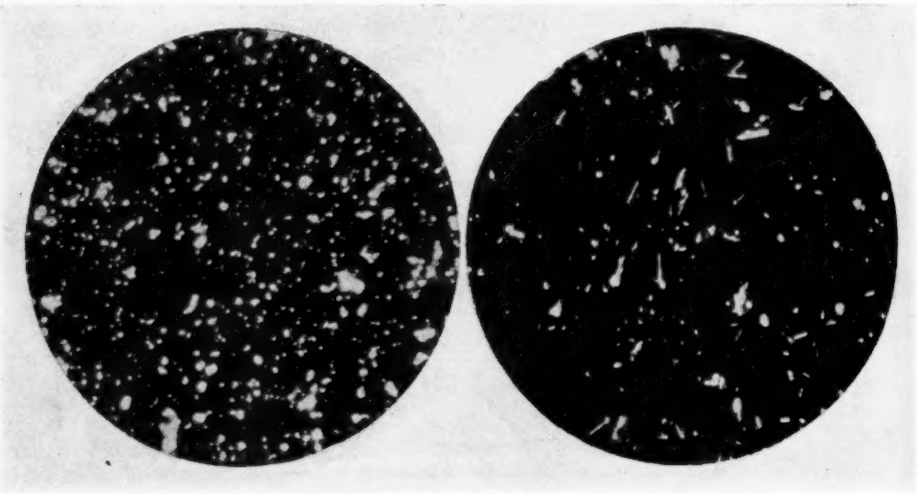

FIG. 13.—Zinc oxides (×1000).

Such observations indicate that, to be useful for the rubber technologist, a report on an unknown pigment sample must include the fullest possible information on the particle shape as well as the average particle size. To obtain this information on pigments with particles above the limit of resolution is relatively simple. The percentage of particles which are acicular may be readily estimated when the usual preparation[12] is examined in a dark-field microscope. When a pigment sample is composed principally of thin plates, as in some samples of clay, for example, it is often desirable to rub out on a slide a small amount of the pigment in an oil having a high refractive index. (A thick mixture of clarified cassia oil and tolu balsam, n = about 1.61, is satisfactory.) When this preparation is then examined in dark-field, the slight flow of the particles aids in securing an accurate idea of the predominant particle shape. With particles below the resolving power, since the direct observation of shape is of course not possible, the Szegvari azimuth diaphragm will be found useful.

This discussion has emphasized that the microscopic laboratory has the responsibility of providing precise, rapid, and useful information on particle size and shape for all divisions of the factory. The methods which have been

described make it possible to maintain that efficient operative function. Rapid operation by these methods yields more satisfactory results than can be obtained by hours of measuring particle sizes by the laborious methods described in the literature. Many of the unsatisfactory conclusions in the attempted utilization of particle size measurements have resulted from the complications and tediousness of the method used. There are only three essential conditions to be fulfilled: good preparations, perfect optical conditions, and a trained eye and brain. Accurate conclusions of the effect of pigment particles in rubber may then be drawn from microscopic observation.

CONTROL OF FACTORY PROCESSING

To the colloid chemist the term "dispersion" denotes the degree of subdivision of the particles in a suspension or a sol. To the rubber technologist dispersion or degree of dispersion denotes the extent to which the individual particles of a pigment are wet by and covered with rubber. The microscope provides the best direct means of determining the degree of dispersion of a pigment in a rubber stock. Various procedures have been described for preparing samples for the microscopic study of dispersion[22]. The method developed and described by Roninger[24] is unique in its interesting application of metallographic methods to the study of rubber articles. The advantages of this method in the study of dispersion of pigments in rubber have been further investigated in the New Jersey Zinc Company Research Laboratory[25].

The usefulness of any method depends on the correlation between the microscopic appearance of a small sample and the gross properties of a large factory batch or finally the finished rubber article. All evidence indicates that the small sample is representative of the whole.

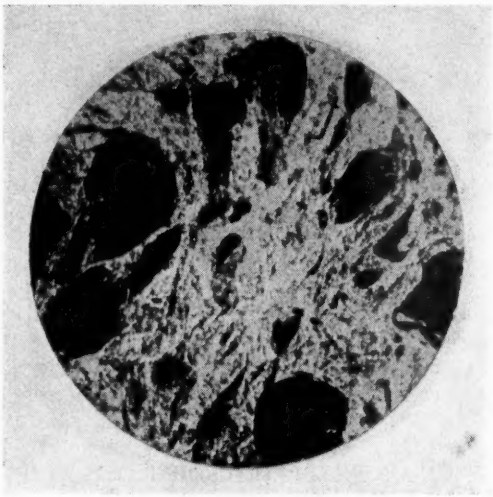

FIG. 14.—Undispersed agglomerates (×200).

The method described by the author[22] for preparing rubber specimens for microscopic examination of dispersion has one advantage which experience shows to be of extreme practical importance. This superiority resides in the

slight distortion produced in the rubber stock during squeezing, which assists in determining the character of any pigment agglomerates. By employing this method, the actual cause of poor dispersion may be learned, *i.e.*, whether the result of using a pigment having inherent poor dispersibility or of improper or insufficient processing. This method also possesses a distinct advantage in time, since it is possible to prepare a section in 5 minutes or less, where other methods require from 30 minutes to an hour or more.

Until recently what might be termed the grosser aspect of dispersion has been the chief study in this field, *i.e.*, the study of undispersed agglomerates of carbon black[26], zinc oxide[27], etc., ranging in size from a few to several hundred microns, exemplified in Figure 14. In 1938, Park and McClellan[28] summarized the work of a number of investigators, all of whom had suggested more or less specifically that the stiffening which occurs on heating of carbon black-rubber stocks is caused by flocculation of the particles of black. The authors presented microscopic evidence that that flocculation does occur. Figure 15 was obtained according to Park and McClellan's procedure. On the

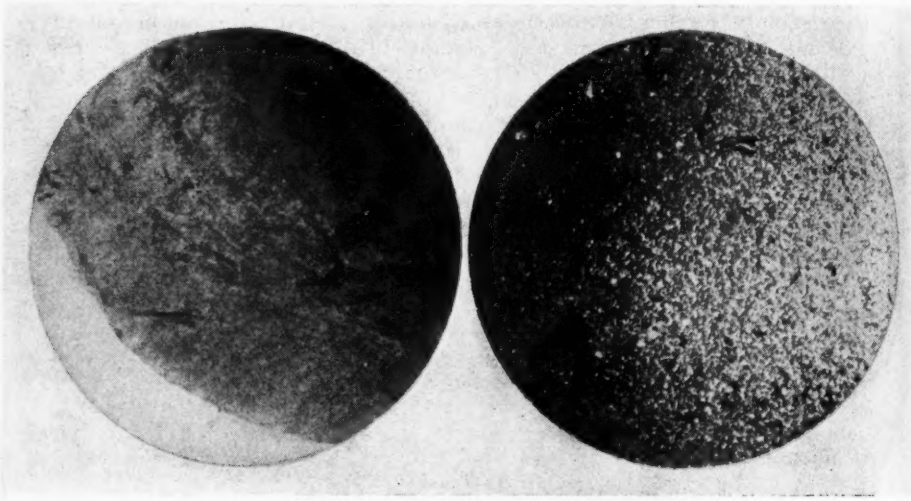

FIG. 15.—Rubber stocks (×200).

left is a rubber stock containing 8 parts by volume of well-dispersed channel gas black; on the right is the same rubber stock after heating for one hour at 135°. This sort of orientation of carbon black particles in rubber may be considered as an aspect of dispersion different from the gross dispersion which has been discussed.

CORRELATION OF PHYSICAL PROPERTIES AND SERVICE PERFORMANCE

The study of pigment dispersion, which vitally affects tread wear, is only one example of the usefulness of microscopic methods in determining and controlling the factors responsible for the service performance of a rubber article.

Wider experience in all phases of rubber goods production and use has also

promoted the application of microscopy to the broader field involving the service performance of all types of rubber articles.

The automobile tire presents an almost limitless field for this kind of study. In the correlation of tread wear, for example, with the particle size of reinforcing pigments, the microscope has made many contributions. In the study of the tire carcass, microscopic methods have afforded the best means of determining the degree of impregnation of fabric by rubber[29] and have been extremely useful in studying the adhesion of rubber to the fabric of the carcass.

Almost all rubber articles are subjected constantly to experimental and development changes to produce goods which give superior service. In studying these experimental articles, microscopic observations provide invaluable information on the cause of premature failure or of extraordinary service.

SOLUTION OF FACTORY DIFFICULTIES

In this important function of microscopy, success depends to a large extent on a wide knowledge of chemical and physical principles, on an abundant experience in factory processes, on a broad acquaintance with many materials, and most of all on ingenuity in applying all this knowledge and experience to the problem in hand. The microscope is not a magic instrument which prints the answer to a question when an object is put on its stage. But if properly used with regard to its optical principles, it often gives the necessary clue which, combined with knowledge and reason, will solve many an otherwise unsolvable problem.

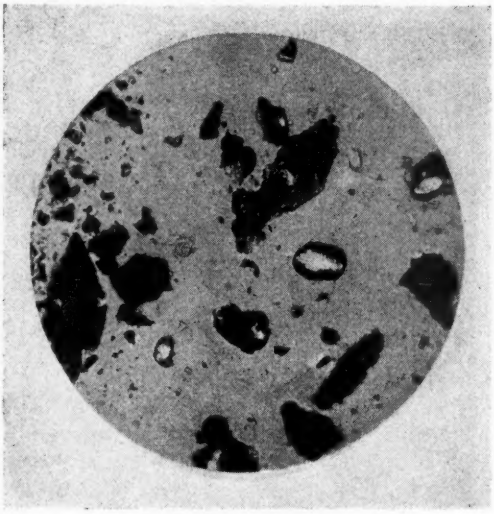

FIG. 16.—Porcelain impurity (×100).

In a certain rubber stock appeared a hard, white, brittle foreign substance, small in amount but very objectionable. A single glance at the crushed substance in polarized light in the microscope (Figure 16) revealed definitely that it was porcelain or a porcelainlike substance. With the character of the impurity established, its source was traced to a raw material and finally to the

porcelain-lined equipment used in the supplier's plant several hundred miles away.

A piece of white stock on which appeared some black streaks (Figure 17, left) was brought into the laboratory. One man claimed that the black streak was grease, while another, responsible for the greasing of the machine where this stock was processed, claimed that the calender operator had confused and mixed two stocks. The microscope made it possible to decide between these two alternatives. A small sample of the black contamination was removed and examined in a polarizing microscope; the appearance (Figure 17, right) proved unquestionably that the black streak was grease. Previous experience had shown that soapstone inevitably is present in high concentration in grease on machinery in a rubber factory, and this provided the clue which solved the problem.

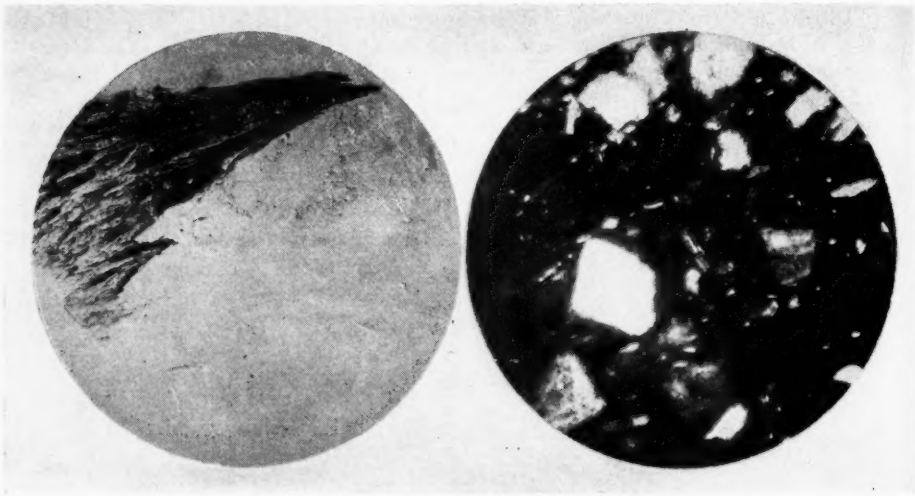

FIG. 17.—Grease impurity.
Left, ×4. Right, ×100.

In many instances of this kind the microscope is invaluable; for it makes possible a quick, positive solution, which in turn enables the operator immediately to correct an unsatisfactory situation.

In the examinations which are frequently required for identifying small amounts of foreign material, practically every facility offered by the microscope or microscopic methods is eventually used. When the observer is familiar with the foreign material, one glance may be sufficient to allow him to identify the substance. If not, he may make qualitative microchemical analyses according to the methods of Chamot and Mason[4], make spot tests according to Feigl, determine optical anisotropy or refractive index on small pieces under the microscope, or utilize some special property such as the fluorescence of the substance.

In many instances, information obtained by ordinary means is almost valueless unless supplemented by information to be obtained with the microscope.

For example, a technical compounder wishes to know what pigments are present in a competitor's article. The stock is analyzed chemically and he receives a report as follows:

Probable Formula	
Rubber	54.50
Softeners	6.50
Total S	3.00
ZnO	4.00
Carbon black	14.00
$CaCO_3$	10.00
$BaSO_4$	8.00
	100.00

With this information alone, it would still be an almost endless task to reproduce the stock because there are several zinc oxides, carbon blacks, whitings, and barium sulfates available for use in rubber. The stock is examined under the microscope and the specific kind of the several materials are determined. The final report then reads as follows:

Probable Formula	
Rubber	54.50
Softeners	6.50
Total S	3.00
American process zinc oxide	4.00
Gastex	14.00
Byproduct whiting	10.00
Blanc fixe	8.00

Obviously the compounder now possesses definite information which, because more accurately defined, makes his task simpler. [Geohegan[30] describes the importance of similar information in the paper mill.]

Fig. 18.—Siliceous impurity (×4).

Sometimes microscopical observation alone, with its possibility of securing a roughly quantitative idea of the pigment present, provides sufficient information for the technical compounder to begin the problem of reproducing a stock with the desired properties.

Microscopical studies must often be supplemented with knowledge outside the domain of optics, in order to finish the clue which will solve a difficulty.

Sheet packing occasionally showed annoying white streaks (Figure 18). The foreign material was examined microscopically and found to be a siliceous material similar to clay. This fact alone did not solve the problem, but by observation of the manufacturing operation the essential clue was discovered.

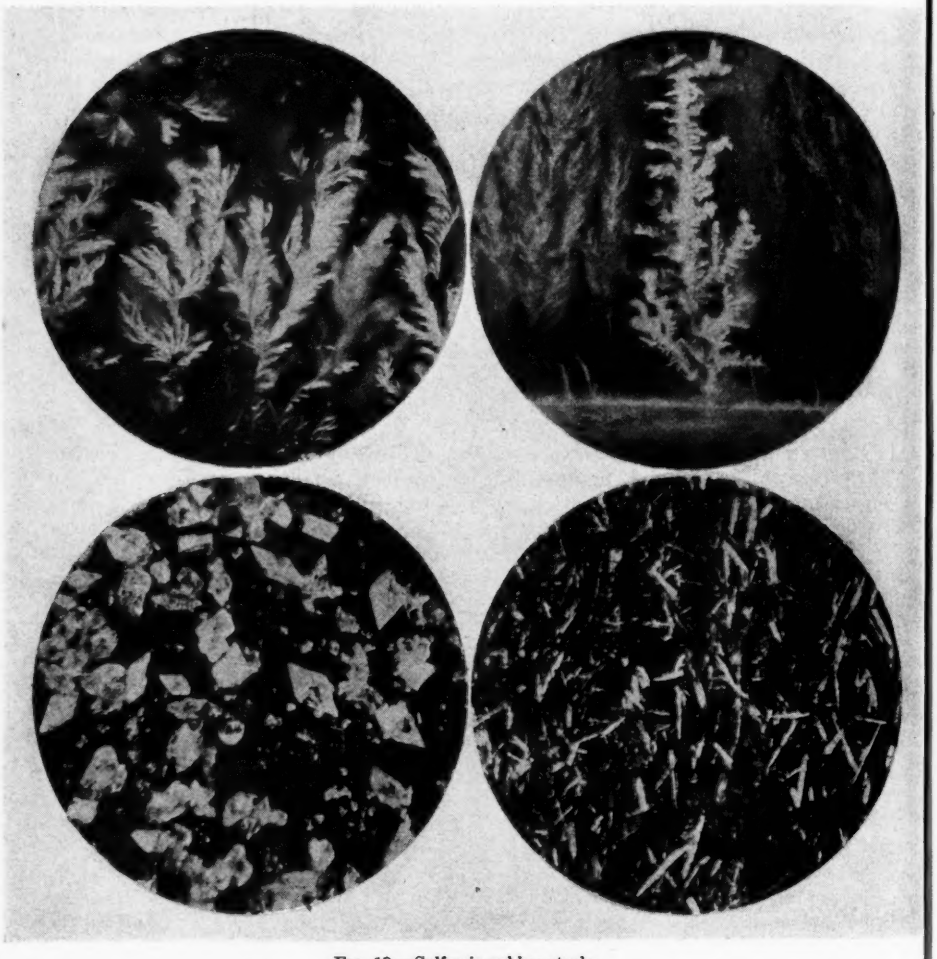

FIG. 19.—Sulfur in rubber stocks.
Upper, ×20. Lower, ×50.

In producing this article a thin layer of an aqueous graphite paste was spread on its surface. As this paste dried, the siliceous particles in the graphite, being preferentially wet by the water, were carried to the surface. This siliceous matter, when dry, appeared as a white streak on the graphite-coated surface. The difficulty was eliminated by substituting a dispersion medium more compatible with graphite than with silica.

Technical men are interested in the subject of bloom. The steps which occur in the development of bloom have been described[31]. Bloom can and does occur in both uncured and cured rubber. The accompanying photomicrographs of sulfur in a cured "pure gum" compound (Figures 19 to 21) were made to illustrate the steps in the development of bloom.

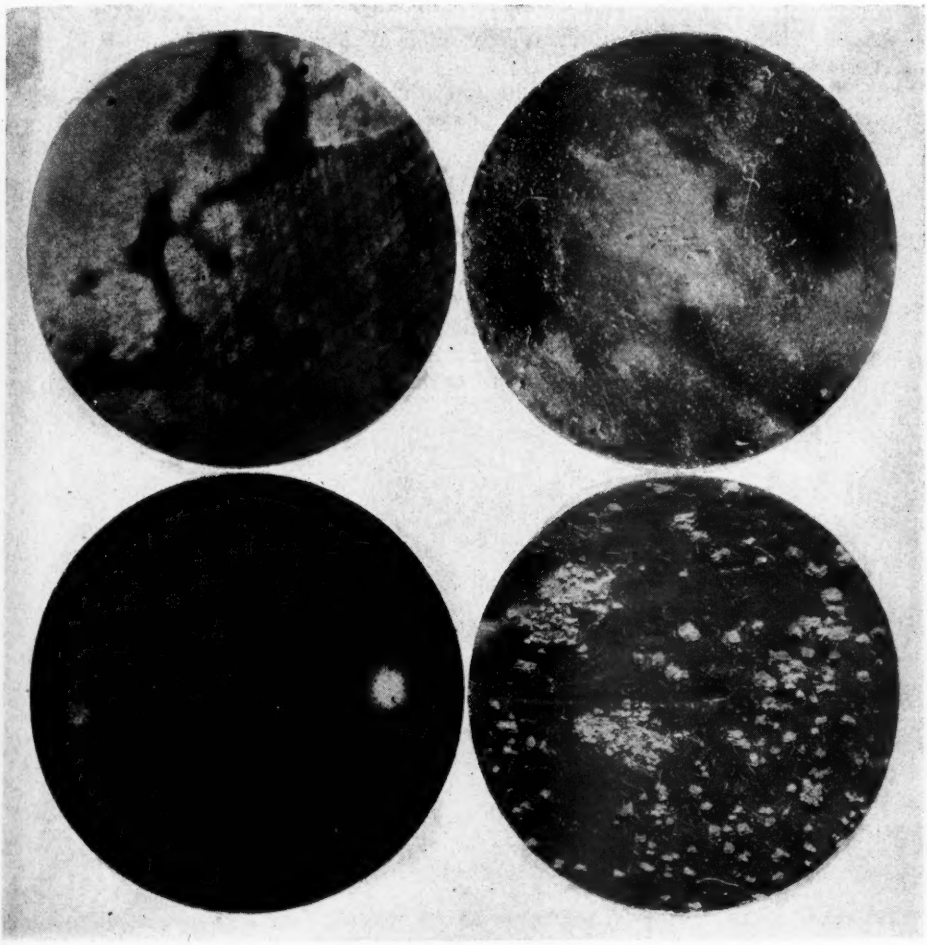

FIG. 20.—Bloom in rubber stocks.
Upper left, ×4. Upper right and lower, ×50.

After a rubber stock is cured, the sulfur in excess of that actually soluble in the rubber precipitates in small particles throughout the mass. Solution of the small particles next occurs, followed by diffusion through the rubber and growth of the larger particles, which are dendritic in form, as shown in Figure 19 (upper left). This Ostwald ripening continues, and in the next stage (upper right) the form is still dendritic, but the separate crystals making up the branches on the central staghorned tree are larger than those in the more

delicate formations. At this stage, diffusion to the surface commences—note that the relatively massive growths of Figure 19 (upper right) are connected to the surface of the sheet—and crystals of sulfur begin to appear on the surface. Eventually this sheet of rubber becomes perfectly clear inside, and all its excess sulfur crystallizes on the surface in the form of perfect rhombs (lower left). Any bloom on rubber, whether sulfur, age-resister, or other material, eventually develops as perfect crystals characteristic of the chemical composition. Figure 19 (lower right) is an example of an age-resister bloom, showing perfect crystal form.

Bloom is seldom desired, and its appearance usually indicates that a material has been incorrectly used or a process has not been properly conducted. Because a bloom usually consists of one pure chemical substance, its identification may be accomplished by determining one or more physical or chemical properties which are characteristic of that substance. Melting point, refractive index, qualitative chemical tests, solubilities, and crystal form may be used for identification. Since the actual quantity of bloom is generally small, the identifying procedure is executed either with the microscope, *e.g.*, refractive index measurements, or by a spot test method.

A bloom sometimes causes some defect in the rubber article on which it appears—for example, the cause of peculiar bad aging in small isolated areas on a colored thin sheet article, evident to the naked eye (Figure 20, upper left),

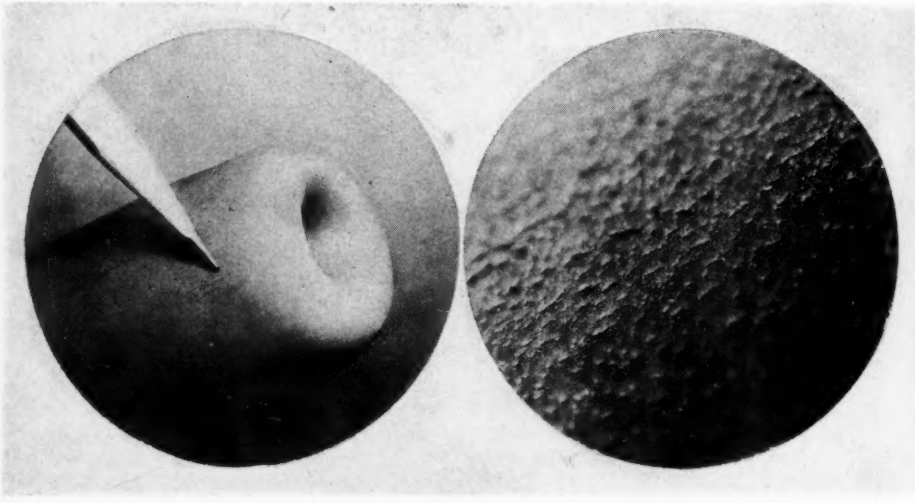

FIG. 21.—Identification of bloom.
Right, ×50.

was investigated. Immediately after cure, some small dark spots could be observed on the surface, and it had been concluded the dark spots were evidence of local high concentration of color. Examination under the microscope disclosed new and important facts. By reflected light it was found (upper right) that the spots were dark, but by transmitted light (lower left) the spots appear lighter than the surrounding area. This indicated, not a high concentration of the coloring pigment, but rather an excessive amount of some colorless substance which had pushed the coloring pigment aside. This substance

was probably either sulfur or accelerator. By a microscopical examination of the uncured stock at high magnification (lower right) it was observed that sulfur had bloomed profusely in small areas. This fact, which had not been disclosed by ordinary methods of observation, explained the poor local aging. At the beginning of the cure, *i.e.*, when the rubber stock came in contact with a hot mold, the stock cured in these bloomed areas before the sulfur could become uniformly distributed by migration. Local overcuring consequently resulted. Knowing this explanation, it became possible to take proper measures to eliminate the cause.

Another case illustrates how one simple, accurate observation in the microscope may be sufficient to provide the clue which solves a difficulty. The article in Figure 21 (left) was apparently bloomed, and a technical compounder requested an identification of the bloom. Observation under a Greenough binocular microscope showed that the condition was not a bloom at all. It was disclosed that the article had been turned inside out, and had been in bright light. Under the influence of the stretching and of the light, the surface had cracked rapidly, leaving small fibers of the rubber stock across the cracks (Figure 21, right). These small threads reflected a relatively large amount of light, giving a whitish appearance much like bloom; the error in analysis by naked eye observation alone was unavoidable.

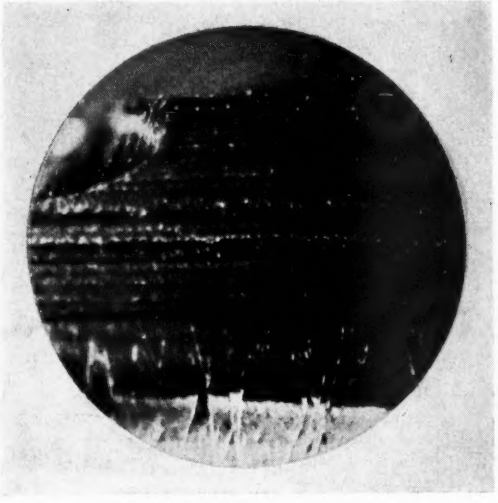

FIG. 22.—Failure due to cut (×20).

Occasionally a customer returns a product with some complaint about its quality. Such a case occurred with a certain article which had presumably failed at a lamination. Careful microscopic observation of the failure (Figure 22) showed conclusively that the article had not failed but had been cut, probably accidentally; under the microscope the knife marks were plainly visible and the crack showed an appearance entirely different from that of a failure at a lamination.

Another case resulted in the deducing of an unusual chain of chemical reactions from one primary fact discovered microscopically. A certain lot of

sheet packing had apparently developed mildew to an annoying extent. The white, fibrous efflorescence on the surface (Figure 23) unquestionably appeared like mildew to the eye, and still looked like mildew when it was examined in a Greenough microscope at 20 or even 100 diameters. When, however, the material was removed, mounted, and examined at higher powers, there were found no spores or oil sacks which are characteristic of mildew. Examination

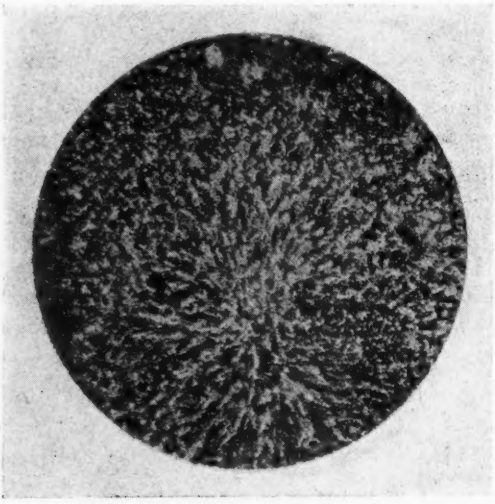

FIG. 23.—Sheet packing (×50).

with polarized light disclosed an abundance of double refracting prisms, which immediately suggested calcium sulfate ($CaSO_4 \cdot 2H_2O$); these, however, could not have been present in the original composition. The identity of this postulated material was confirmed both by the extinction angle of the crystals and from qualitative microanalysis. Knowing the composition of the efflorescence still did not solve the mystery of its presence, but a combination of facts, some already known and some acquired at the time, made a logical, if unusual, chain of reactions fit into the final result. On the surface of the sheet, some sulfur bloom had undoubtedly developed. The sheeting for a time had been stored in a roll, slightly damp, and in a warm place. Under these conditions the bloomed sulfur had oxidized, eventually forming dilute sulfuric acid with the moisture present, which in turn gradually reacted with the whiting in the sheet, forming calcium sulfate which eventually crystallized out in the form of more or less perfect prisms.

Articles returned by the customer for adjustment sometimes prove to be of a competitor's manufacture, and microscopical methods are often invaluable in disclosing this fact. For example, two samples of white thread were brought into the laboratory to determine whether they were of the same or different manufacture. The samples were first examined under a low-power microscope, and Figure 24 (left) shows clearly that their surface appearances were different. Microsections were made of two samples (Figure 24, center and right), and again a difference could be observed; the pigmentation was not the same in particle size and possibly not in concentration. Finally a micro-

qualitative analysis was made on the ash, and the compositions were found to be entirely different. One was a standard Goodrich product; the other was proved definitely to be that of a competitor.

Another case of a similar nature shows that even the science of deduction may be enlarged to unusual limits with the aid of the microscope. Some small cups were returned with the complaint that they showed premature aging. This seemed to the technical compounder who was responsible for their quality

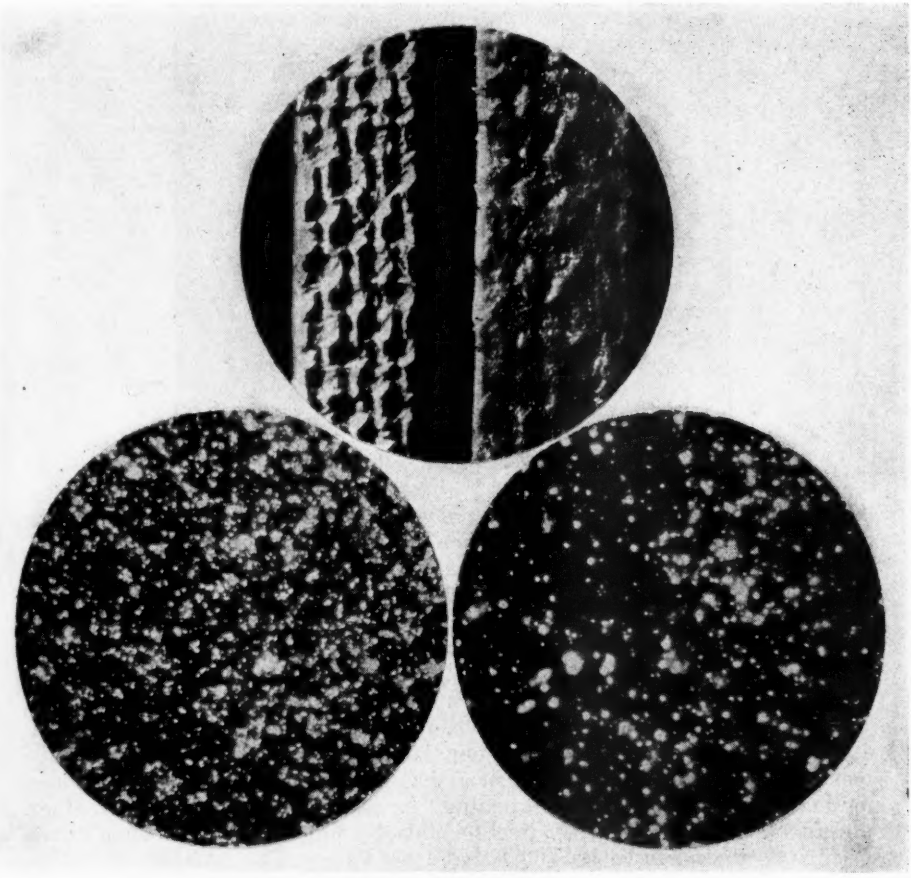

FIG. 24.—White thread.
Center and right, ×1000.

to be inconsistent with this knowledge of their aging behavior; however, the article, shown on the left in Figure 25, unquestionably was badly aged when compared with the new cup shown on the right. In the effort to find out whether the aging was premature, the fact was uncovered that the source of zinc oxide used for the rubber stock for this cup had been changed more than 2 years previously. Microsections were made and microscopical examination of the old and the new proved positively, from the character of the particles of the zinc oxides, that the returned sample was more than 2 years old. The

fact was presented to the customer that the article had been lying on his shelf for that length of time and he agreed that the aging was not excessive.

This list of case histories in which problems, apparently not solvable by other means, have been solved by means of the microscope, could be largely extended. Space does not permit illustrating, by examples, every facility which the microscope affords. Frequent questions arise concerning the com-

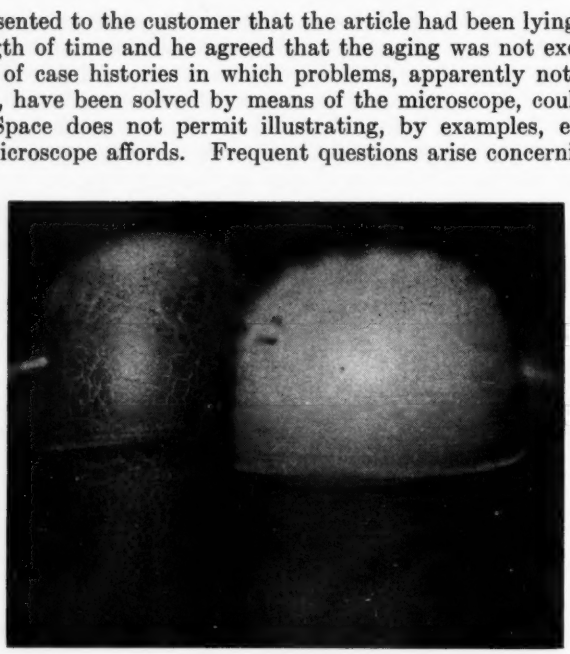

FIG. 25.—Aging of small cup.

patibility of rubber with rubberlike materials, such as Neoprene or Thiokol; the examination of a suitable preparation in a dark-field microscope is probably the most direct and positive means of determining the existence of distinct phases and certainly one of the most rapid. Microcataphoresis methods have been used in the study of certain pigments and latex. Some problems require the use of metallographic methods; in many cases where vertical illumination is used polarized light is serviceable. Fluorescent microscopy is an elegant method, revealing information which is otherwise unobtainable[32].

Although many problems possess traits in common, a large proportion of cases display new features which require strictly individual and original treatment. This paper presents evidence that the microscope and microscopic methods disclose invaluable information, far less readily obtainable by other means and indeed frequently unobtainable by procedures other than those peculiar to the microscope.

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DENSITY MEASUREMENTS ON SYNTHETIC RUBBERS *

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For many purposes the density of a material need be known with an accuracy of only a few per cent. For many materials the density of one sample may differ from that of another by this amount, and no useful purpose may be served by making more precise measurements on individual samples. In natural rubber, the densities of different samples have been shown, in a compilation[1] of twenty-one values, to lie with two exceptions between 0.905 and 0.919 gram per cc. at 25° C. The variations probably represent real differences in the samples and not accidental errors of observation. Since one can seldom know exactly the origin and subsequent treatment of a sample of natural rubber, there is little value in increasing the precision of measurement.

Synthetic rubbers, on the other hand, can be regarded as usually produced under conditions which are much better controlled and known. It is logical, then, to measure the density with greater precision and to hope to be able to ascribe significance to its variations from one sample to another. The present work is concerned with the development of a method for preparing specimens of synthetic rubber in a form suitable for precise measurements of the density, the actual measurement by the method of hydrostatic weighings, and a presentation of the results for most of the varieties of synthetic rubber now of commercial importance in the United States.

PREPARATION OF SPECIMENS

Samples of synthetic rubber, as received from the manufacturer, were never found to be in a form suitable for precise measurements of density. Even where there appeared to be no entrapped air and the surfaces seemed to be relatively smooth, moulding produced specimens yielding higher and much more consistent values. Since a number of precautions are necessary to obtain good specimens, the method of preparation will be described in some detail. The ease of preparation of specimens was considerably affected by their rheological properties, and there was a wide difference between the different types of synthetic rubber in this respect. In many cases not all the precautions described were necessary.

The surface of the material was first examined for the presence of talc or other powders which might have been dusted on it. Vigorous scrubbing with a brush under running water usually removed the powders. This was followed by drying in a vacuum desiccator.

About 7 cc. of the material were then sheeted out by several passes between warm mill rolls. The sheet, usually between 0.010 and 0.015 inch thick, was folded over itself several times and placed in a mould consisting merely of a sheet of metal with a single rectangular opening. The specimen and mould were sandwiched between aluminum sheets and placed in the vacuum chamber shown in Figure 1. The chamber was made of steel, and included a movable

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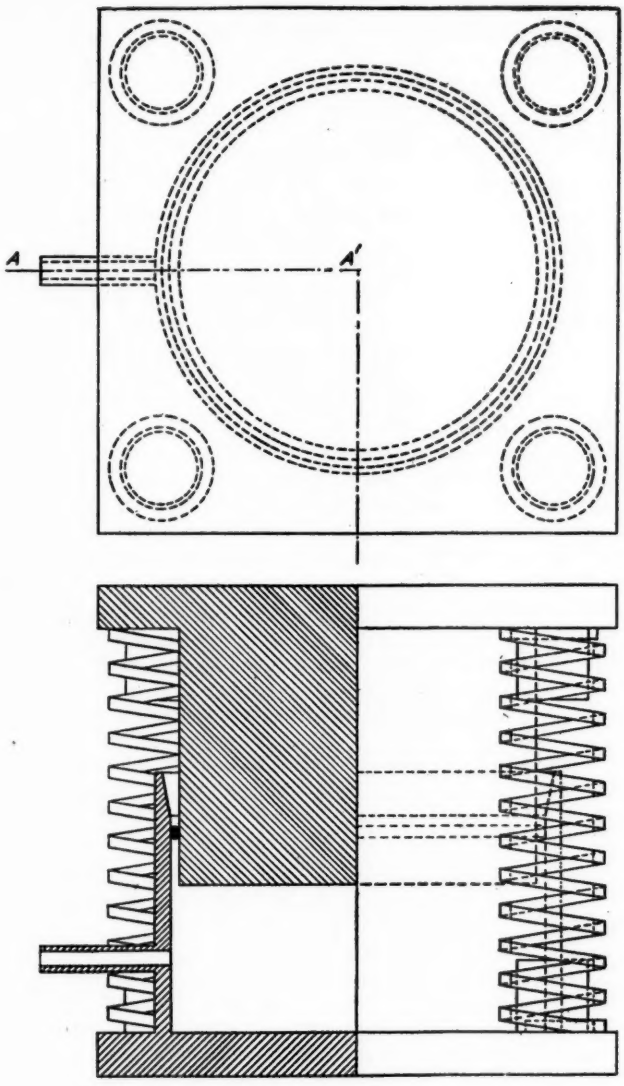

FIG. 1.—Vacuum chamber.

Section AA' is shown at the lower left. The cross section of the rubber gasket is marked in black. The plates at the top and bottom of the chamber are 180 mm. square. The diameter of the piston is 125 mm.

piston of the same material, with about 3.5-mm. clearance between chamber and piston. The piston was sealed by a toroidal rubber gasket which did not slide on the piston or side walls, but rolled as the piston moved up or down. The gasket was about 100 mm. in diameter and about 4 mm. in section diameter. Four springs at the corners of the plate at the top of the chamber exerted an upward force on the piston. They were so chosen that, when the

chamber was evacuated, atmospheric pressure on the piston moved it downward about half its full stroke, compressing the springs. The chamber was then placed between the platens of a vulcanizing press, and the platens were moved together sufficiently to make contact with the top of the vacuum chamber and to compress the springs a little more, but not enough to move the piston far enough to cause appreciable flow of the material. In this manner the material was heated for 1 or 2 hours at about 130° C, under vacuum. Next, the platens of the hydraulic press were brought somewhat closer together to cause some flow of the material. After several stages of increase of hydraulic pressure, the full force of 50 tons was finally applied to the vacuum chamber. After 1 or 2 hours to allow for further flow, the steam was turned off, and the press allowed to cool, with the hydraulic pressure still applied. Finally air was admitted to the chamber and the specimen removed.

Some materials could be separated only with difficulty from the aluminum sheets above and below the specimen. In some cases mould lubricants, such as Carbowax, when used in small amounts, were found to eliminate this difficulty. Carbowax is water-soluble, and was readily removed from the surface of the specimens by washing. Chemigum-I and some other materials were separated from the aluminum most easily when cooled to about 0° C.

The dimensions of the sheets made in this manner were about $60 \times 60 \times 1.6$ mm. ($2.4 \times 2.4 \times \frac{1}{16}$ inch). Each sheet was cut into three specimens with scissors. In cutting, care was taken to discard portions of the sheet with surface irregularities and to cut with a single stroke so as to give a smooth edge. The specimens were sufficiently thin so that with most of the materials inhomogeneities, if present in the interior, could easily be seen when the specimen was held up to the light. Specimens with inhomogeneities were discarded.

MEASUREMENT BY HYDROSTATIC WEIGHING

The measurement of density by the method of hydrostatic weighing required the use of a sinker, since many of the materials were lighter than water. The sinker employed in the present work was a tin disk about 20 mm. in diameter and about 4 mm. thick, to which the specimen could be conveniently attached. The plane of the specimen was kept approximately vertical to diminish the resistance to the motion through the water during weighing. A 5-mil platinum wire suspended the sinker from the hook above the pan of the balance. The water was contained in a beaker supported on a small wooden bridge over the pan of the balance.

Before each set of measurements, the platinum wire was washed with water containing talc or soap so that it could be wetted readily and the effects of surface tension minimized. The specimen was next placed in the water and then removed. Usually air bubbles were observed clinging to the specimen, particularly on the edges. These were rubbed off with the fingers, and the specimen was replaced in the water. The operation was repeated, if necessary, until no air bubbles could be seen. Weighings were carried out with an ordinary analytical balance to 0.1 or 0.2 mg.

The quantities observed and the method of computation are illustrated by the typical data and calculations shown in Table I. The temperature seldom differed from 25° C by more than 2° or 3°. Consequently it was seldom necessary to have accurate values for the rate of change of density of the sample with temperature. In some cases the rate was determined from measurements of density at two different temperatures, and in others it was obtained from

independent measurements of the expansivity by dilatometers. In few cases was the value significantly different from 620×10^{-6} gram cm.$^{-3}$ (° C)$^{-1}$, the value reported (*1*, *2*) for natural rubber.

TABLE I

TYPICAL DATA AND CALCULATIONS

	Buna-S	Neoprene-GN
Weights, grams[a]		
A. Specimen	1.1573	2.0577
B. Sinker in water	11.1355	11.1370
C. Specimen and sinker in water	11.0497	11.5256
D. Specimen in water	−0.0858	0.3886
E. Loss in water	1.2431	1.6691
F. Specific gravity[b]	0.9310	1.2328
G. Temperature[c] (° C)	26.6	24.5
Densities, grams per cc.[d]		
H. Water at temp. *G*	0.9966	0.9972
I. Sample at temp. *G*	0.9279	1.2293
J. Sample at 25° C	0.9289	1.2290

[a] *A*, *B*, and *C* were measured directly; $D = C - B$; $E = A - D$.
[b] $F = A/E$.
[c] *G* was measured directly.
[d] *H* was obtained from tables; $I = FH$; $J = I[1 + \alpha(G\text{-}25)]$, where α = rate of change of density of sample with temperature.

RESULTS

The results of measurements of the densities of eighteen different varieties of synthetic rubber are given in Table II. With the exception of the sample of Buna-S described in footnote [b], they were all of commercial origin, and are considered typical of present-day commercial production in the United States. Most of them were received during the spring and summer of 1942. The values shown are, in most cases, the means of the measurements on six different specimens, three cut from each of two mouldings. Additional specimens were moulded when any of the individual results differed from the mean by more than about 0.05 per cent. In a few cases only four specimens were used, and in other instances more than six were made.

Unpublished observations in this laboratory have shown that crystallization, with an accompanying increase of density, occurs at room temperature with Neoprene-CG, Neoprene-E, Neoprene-GN, and Thiokol-A. Consequently, with these materials care was taken to make the measurements of density as quickly as possible after the heating. All measurements on Neoprene-CG, which crystallizes most rapidly, were made within one-half hour after heating. Crystallization effects do not seem evident with any of the other varieties of synthetic rubber listed in Table II. However, it was found that a number of the synthetic rubbers showed elastic recovery effects, which made it preferable to take the measurements soon after moulding. This elastic "memory" led to the development of roughened surfaces and sometimes to vacuoles, which brought about a decrease in the apparent density after a few days. The results under these conditions were always much less consistent than those obtained from observations made immediately after moulding. The necessity for moulding under vacuum did not seem to be so great for those materials in which the "memory" effects were small.

It should be noted that, although the values given represent the means of observations on a number of specimens, the specimens were made from only one sample of each variety. Consequently this work furnishes no information

TABLE II

DENSITY VALUES AT 25° C

Type[a]	Name	Manufacturer	Density (grams per cc.)
I	Neoprene-CG	Du Pont Co.	1.2307
I	Neoprene-E	Du Pont Co.	1.2384
I	Neoprene-FR	Du Pont Co.	1.1406
I	Neoprene-GN	Du Pont Co.	1.2290
IIA	Buna-S[b]	Firestone Tire & Rubber Co.	0.9291
IIA	Buna-S[c]	Firestone Tire & Rubber Co.	0.9358
IIA	Buna-S	U. S. Rubber Co.	0.9369
IIA	Buna-S	Standard Oil Development Co.	0.9390
IIA	Chemigum-IV	Goodyear Tire & Rubber Co.	0.9391
IIA	Hycar-OS-20[d]	B. F. Goodrich Co.	0.9385
IIA	Hycar-OS-30[e]	B. F. Goodrich Co.	0.9303
IIB	Chemigum-I	Goodyear Tire & Rubber Co.	1.0135
IIB	Hycar-OR	B. F. Goodrich Co.	0.9992
IIB	Perbunan	Standard Oil Development Co.	0.9684
IIB	Thiokol-RD	Thiokol Corp.	1.0564
III	Thiokol-A	Thiokol Corp.	1.5983
III	Thiokol-FA	Thiokol Corp.	1.3298
IV	Butyl-B-1.45	Standard Oil Development Co.	0.9175

[a] Type I = chloroprene polymers and related polymers. Type II = butadiene copolymers; A = copolymers with styrene (Buna-S type), B = other butadiene copolymers, chiefly copolymers with acrylonitrile. Type III = organic polysulfides. Type IV = isobutene copolymers.

[b] Prepared in a laboratory polymerization with a minimum quantity of materials other than butadiene and styrene. Analysis of this sample is said to give: ash 0.09%, free fatty acid 0.51, phenyl-β-naphthylamine 0.50, acetone extract 4.01.

[c] Contains about 4.5% of free fatty acid and 2% of phenyl-β-naphthylamine; ash content about 0.4% (according to information from J. N. Street).

[d] "A special type of butadiene-styrene copolymer made by the process developed by the B. F. Goodrich Co. It is made from butadiene and styrene in the same ratio as is used in the manufacture of Hycar-OS-30. It is stabilized with 2% of Stalite antioxidant", according to information from W. L. Semon.

[e] "A butadiene-styrene copolymer of the type which will be made in government-financed plants. It contains not only the rubber hydrocarbon but approximately 4.5% of fatty acid. It is stabilized with 2% of Stalite antioxidant", according to information from W. L. Semon.

regarding the variation in density from different batches or runs of the same manufacturer. The method of measurement described here should be sufficiently precise to find application for this purpose, and might be used as a control method.

ACKNOWLEDGMENT

Grateful acknowledgment is made of the coöperation of the companies listed in Table II in furnishing samples of synthetic rubber on which the observations were made. Especial thanks are due to J. N. Street for the preparation and analysis of the polymer described in footnote[b] to Table II.

REFERENCES

[1] Wood, *Proc. Rubber Tech. Conf. London*, 1938, p. 933; RUBBER CHEM. TECH. 12, 130 (1939).
[2] Wood, *Proc. Rubber Tech. Conf. London*, 1938, p. 933; RUBBER CHEM. TECH. 12, 130 (1939); Curtis, McPherson and Scott, Natl. Bur. Standards, Sci. Paper 22, 383 (1927).